ENVIRONMENTAL MONITORING OF MCPA IN RELATION TO ORCHARD CONTAMINATION

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CALIFORNIA DEPARTMENT OF FOOD AND AGRICULTURE
CONTRACT NO. 7458

MARCH 16, 1981

EH 88-9

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SUMMARY

MCPA (4-Chloro-2-methylphenoxyacetic acid) is a major herbicide used on California rice and other grain crops. In 1979, over 566,000 pounds of MCPA salts and esters were applied in the state, an increase of 60% since 1971. Use data show that Colusa County consistently received the largest application, followed by Sutter and Butte Counties, and that the majority of applications were associated with the river systems.

MCPA usually is applied by air as an aqueous solution of the dimethylamine (DMA) salt which is surprisingly pure (>98%). Although rather stable in a dark container, MCPA/DMA spray evaporates quickly to a sticky semisolid which decomposes within a few days in sunlight to give chlorocresol (4-chloro-2-methylphenol) and other identified products.

Analysis of the ambient atmosphere during and after spraying (of rice fields) showed MCPA decreasing and the proportion of chlorocresol increasing with both time and distance. However, both were detected at ng/m^3 levels in the air of adjacent orchards, upwind at the time of spraying, as well as in areas several km distant from known application. Foliage residues of MCPA were detected in the orchards, with a maximum value of 0.45 ppm (on trees adjacent to the spray application); no MCPA was detected in similar samples collected 3 months after the application. Significant amounts of MCPA failed to reach target fields.

No obvious symptoms of phytotoxicity were observed on the almond, pistachio, or walnut trees where MCPA residues were detected, and review of pertinent literature indicates that intoxication of humans or animals by MCPA at the observed levels is unlikely. The long-term fate and effects of MCPA and chlorocresol remain unconfirmed.

I. INTRODUCTION

Project Background

4-Chloro-2-methylphenoxyacetic acid (MCPA) long has been a major herbicide in California and throughout the world (Table 1). The 1971 Pesticide Use Report of the California Department of Food and Agriculture indicates that 353,169 pounds of MCPA salts and esters were applied during that year; by contrast, the 1979 Report shows application of 566,603 pounds, of which 535,169 pounds (94.5%) was in the form of the dimethylamine (DMA) salt.

Most of the MCPA (79%, or 448,089 pounds in 1979) was applied for broadleaf weed control in rice, although another 90,651 pounds (16%) was used on barley, oats, and wheat. In fact, the herbicide is used because of its selectivity in affecting broadleaf weeds at application rates which cause little or no injury to the small-grain species. However, valuable broadleaf ornamental and crop plants also may be damaged if accidentally exposed to MCPA spray, and concern was expressed by growers that herbicide applications to rice might damage adjacent almond and pistachio orchards.

MCPA came into widespread use in the late 1940's. Despite its extensive use, comparatively little pertinent information exists on its environmental movement, breakdown, and metabolism. Previous work in this Department (Soderquist and Crosby, 1975) examined the distribution and fate of MCPA in rice field water, mud and plants following aerial spraying of the dimethylamine salt. Most (77%) of that reaching the field resided initially in the water. As this chemical is a relatively strong acid (pk_a 3.2), no significant volatilization occurred at the alkaline pH of the field, and dissipation was due to microbial and photochemical action. Mud initially contained 9% and plants 7% of the applied MCPA, but the amount declined sharply over a period of a few days due to metabolism.

However, only 45% of the expected application (980 g/ha as MCPA) could be accounted for on Day 0, and it must be assumed that at least a part of the missing material entered the atmosphere as spray drift. Earlier Russian reports (Tupeeva, 1967); Uporova and Shtiler, 1973) described only rather crude methods for sampling and colorimetric analysis of MCPA in air, and no further investigation of MCPA drift appears to have been reported in the literature. Although many analytical methods have been provided for residue analysis of MCPA in herbaceous plants (see Sattar and Paasivirta, 1979), and the MCPA plant metabolites have been identified (Loos, 1975), the only woody species for which data exist are alder and birch in Scandinavia (Lund-Hoie, 1973; Eronen et al., 1979). The recent use of high-pressure liquid chromatography (HPLC) for the analysis of MCPA-amine recently was described (Stevens and Grorud, 1979; Grorud and Stevens, 1980), but the environmental fate of MCPA was not investigated.

In 1978, the California Rice Research Board and the California Department of Food and Agriculture separately approached the University of California to conduct research which would ascertain the stability of the MCPA-amine formulations and establish what chemical residues to look for, develop the necessary methods to sample, detect, and measure them, field-test the methods for use in environmental monitoring, and provide information about the environmental consequences of MCPA spraying. This report describes the results of that jointly-funded project.

Objectives and Work Plan

The stated objectives were as follows:

(1) To identify the chemical residues resulting from agricultural spray applications of MCPA;

(2) To develop analytical methods to sample, detect, and measure the principal MCPA residues in air and leaf samples;

(3) To test-monitor MCPA residues in the Butte County area in relation to their possible contamination of non-target crops;

(4) To provide information on the environmental fate of MCPA.

The work was divided into four components. The Information Component (Dr. Li), in collaboration with CDFA, initially provided economic and pesticide use data for Butte, Colusa, Glenn, Sutter, and Yuba counties and later for Placer, Sacramento, and Yolo; they also provided computer mapping of applications and other bibliographic and technical data. The Chemistry component (Dr. Crosby) determined the chemical composition of the MCPA spray and spray concentrates, the composition of "weathered" spray residue, and the chemical species to be sampled and analyzed.

The Air Analysis Component (Dr. Seiber), in collaboration with CDFA and UCD Agricultural Engineering, developed methods for collection of air samples and their analysis for the chemical species defined by the Chemistry Component; they also provided the necessary meteorological information. The Plant Analysis Component (Mr. Winterlin) developed and applied analytical methods for the identified residues in leaf and other samples.

The coordinated methods and information were tested by monitoring air and leaf residues during and following commercial applications of MCPA to rice in the Butte County area. The investigation was expected to provide (1) tested methods for monitoring MCPA residues in air and plant materials, (2) initial monitoring results for 1979-80 MCPA applications in the selected test area, (3) information on the persistence and environmental fate of MCPA under California

use conditions, and (4) the basis for subsequent estimation of possible toxic hazards of present MCPA applications for non-target crops and humans. Preliminary finding were communicated by conferences and quarterly written reports; this represents the final, comprehensive report.

Acknowledgements

The investigators acknowledge with thanks the contributions of the following UCD personnel: N.B. Akesson, D.E. Bayer, J.B. Bowers, K.P. Downes, M. McChesney, C. Mourer, C.L. Reece, R. Tai, T. Wehner, and J.E. Woodrow. Other contributors are acknowledged in the respective sections.

The research was supported, in part, by the California Department of Food and Agriculture (Agreement 7458), The California Rice Research Foundation, and USDA Regional Research Project W-45.

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STATE OF CALIFORNIA
DEPARTMENT OF FOOD AND AGRICULTURE
QUARTERLY
PESTICIDE USE REPORT JAN-DEC 1979

CHEMICAL COMMODITY	APPS.	POUNDS	ACRES
MCPA, BUTOXYETHANOL ESTER			
BARLEY	14	661.34	1,149.00
WHEAT	6	126.01	160.00
TOTAL		787.35	
MCPA, DIMETHYLAMINE SALT			
BARLEY	226	21,111.83	26,698.80
BEANS	57	3,686.24	3,984.00
CLOVER	1	34.31	38.00
CORN	2	246.73	162.00
FALLOW FARM LAND	1	93.87	154.00
INDUSTRIAL AREAS	1	7.35	6.00
NON-AGRICULTURAL AREAS	6	82.36	147.50
OATS	95	4,535.13	6,655.00
PASTURE/RANGELAND	27	1,042.95	3,603.00
PEAS	31	1,885.09	3,201.00
RICE	2,566	448,088.69	393,602.65
RICE	1	96.00	.08
RIGHTS OF WAY	1	97.87	
TURF	2	97.88	80.00
WHEAT	601	54,060.20	71,243.00
TOTAL		535,168.60	
MCPA, ISOOCTYL ESTER			
BARLEY	54	6,306.96	8,076.00
OATS	2	180.92	240.00
WHEAT	36	2,500.63	3,251.00
TOTAL		8,988.51	
MCPA, SODIUM SALT			
BARLEY	4	349.02	560.50
BEANS	6	417.18	723.00
OATS	5	62.96	178.00
PEAS	16	557.77	1,349.00
RICE	170	19,446.12	21,250.00
SORGHUM	2	57.34	70.00
TURF	1	10.92	10.00
WHEAT	20	756.19	1,500.00
TOTAL		21,657.50	

II. APPLICATIONS OF MCPA AMINE SALTS AND OTHER DERIVATIVES

The only amine salt of MCPA used in Northern California, according to the CDFA Pesticide Use Report, is the dimethylamine salt; other derivatives include the sodium salt, iso-octyl ester, and butoxyethyl ester ("ethylene glycol butyl ether ester"). The 1974-79 use data for Butte, Colusa, Glenn, Placer, Sacramento, Sutter, Yolo, and Yuba counties were graphed by month of application (Appendix I), the annual totals bargraphed (Appendix I), and the monthly and annual totals tabulated in detail (Appendix II).

Colusa County consistently has been the largest user, followed by Butte (and in 1979 Sutter) County (Table 2), although all eight counties registered some use. In recent years, most of the MCPA has been applied as an aqueous spray of dimethylamine salt (Table 2). That the major use comes in June and July is consistent with its principal application as a rice herbicide, although application to small grains during Winter months is reflected in the lower figures for February and March in most of the counties.

There was a subtantial increase in the use of other derivatives in 1979. While there was increased but still small use of butoxyethyl ester on barley, major increases occurred in the use of iso-octyl ester on barley (190% compared to 1978) and wheat (1100% compared to 1978) and with the sodium salt on rice (400% compared to 1978). Increases also were observed for DMA salt on pasture/rangeland, peas, and rice, while the use on wheat declined over 50% according to the CDFA Pesticide Use Reports.

The location of total 1979 MCPA applications was mapped for each county (Appendix III). It is not surprising that applications in Butte, Colusa, Glenn, Placer and Yuba counties were largely restricted to a small section located in the immediate vicinity of waterways. Sacramento county use was more scattered,

while Sutter and Yolo uses ranged throughout the county. This high concentration of MCPA use--primarily on flooded rice along the major river systems--is illustrated in Fig. 1.

The other phenoxy herbicide most used in the eight-county area was 2,4-D (2,4-dichlorophenoxyacetic acid). Although 2,4-D and MCPA can be distinguished by gas chromatography, the chemical properties and phytotoxic symptoms are closely similar. Again, amine salts (especially the DMA salt) represented the principal form, although 2,4-D esters were more important than those of MCPA. Major uses of 2,4-D/DMA were on barley, wheat, and pasture, while esters were used on barley, wheat, and timber land. Almost no 2,4-D was used on rice. Despite this, large amounts of 2,4-D derivatives were applied over the years in the eight counties (Table 3), although recent volume has declined somewhat. The principal use on small grains is reflected in the major applications in February, March, and April (Appendix IV), with Fall application in Butte and Placer counties largely on conifers. On the other hand, significant use occurred during Summer months in all counties but Glenn. The monthly distribution of uses are detailed in Appendix V.

Considering the above statistics, it is most likely that MCPA residues in the environment would be most concentrated in rather narrow bands associated with Sacramento Valley river systems and during the period of June through August. This period, also represents that of highest average temperature and most intense sunlight in the area and might be expected to provide maximum dissipation and degradation of applied pesticides.

TOTAL POUNDS OF MCPA (AMINES) APPLIED IN
EIGHT COUNTIES OF CALIFORNIA

1974 - 1979

COUNTY	1974	1975	1976	1977	1978	1979
Butte	46,517	61,444	66,947	56,124	78,873	85,197
Colusa	46,498	80,401	115,660	148,941	111,627	144,863
Glenn	47,480	62,381	36,171	107,242	66,376	57,431
Placer	2,613	7,278	5,632	4,992	11,221	10,002
Sacramento	4,113	20,301	6,903	7,854	23,121	21,569
Sutter	27,840	62,970	45,970	27,220	65,159	88,230
Yolo	7,765	24,148	16,880	13,114	16,993	32,043
Yuba	6,772	11,259	9,035	9,745	14,147	17,773

TOTAL POUNDS OF MCPA (OTHERS) APPLIED IN
EIGHT COUNTIES OF CALIFORNIA

1974 - 1979

COUNTY	1974	1975	1976	1977	1978	1979
Butte	11,451	2,132	813	48	67	226
Colusa	36,790	3,227	1,729	726	468	1,263
Glenn	8.809	3,130	2,477	647	604	4,176
Placer	1,175	1,452	356	23	37	44
Sacramento	3,471	959	241	276	270	1,388
Sutter	17,891	5,426	3,176	2,050	2,394	7,561
Yolo	9,919	4,191	9,137	1,083	2,734	6,660
Yuba	1,869	0	0	0	0	0

Source: California Department of Food & Agriculture, Pesticide Use Report tapes.

Table 3

TOTAL POUNDS OF 2,4-D (ALL FORMS) APPLIED IN EIGHT COUNTIES OF CALIFORNIA

1974 - 1979

COUNTY	1974	1975	1976	1977	1978	1979
Butte	21,620	32,228	28,936	44,718	20,354	14,078
Colusa	74,327	84,711	48,966	56,164	56,011	74,948
Glenn	89,591	59,529	25,201	36,774	38,929	31,566
Placer	8,128	6,540	8,336	6,214	4,677	3,944
Sacramento	32,311	50,772	47,378	48,919	28,296	35,656
Sutter	35,069	42,296	48,123	30,941	18,595	25,430
Yolo	70,168	95,266	49,656	52,018	52,173	52,268
Yuba	5,679	8,605	6,002	5,854	5,151	4,839

Source: California Department of Food & Agriculture, Pesticide Use Report tapes.

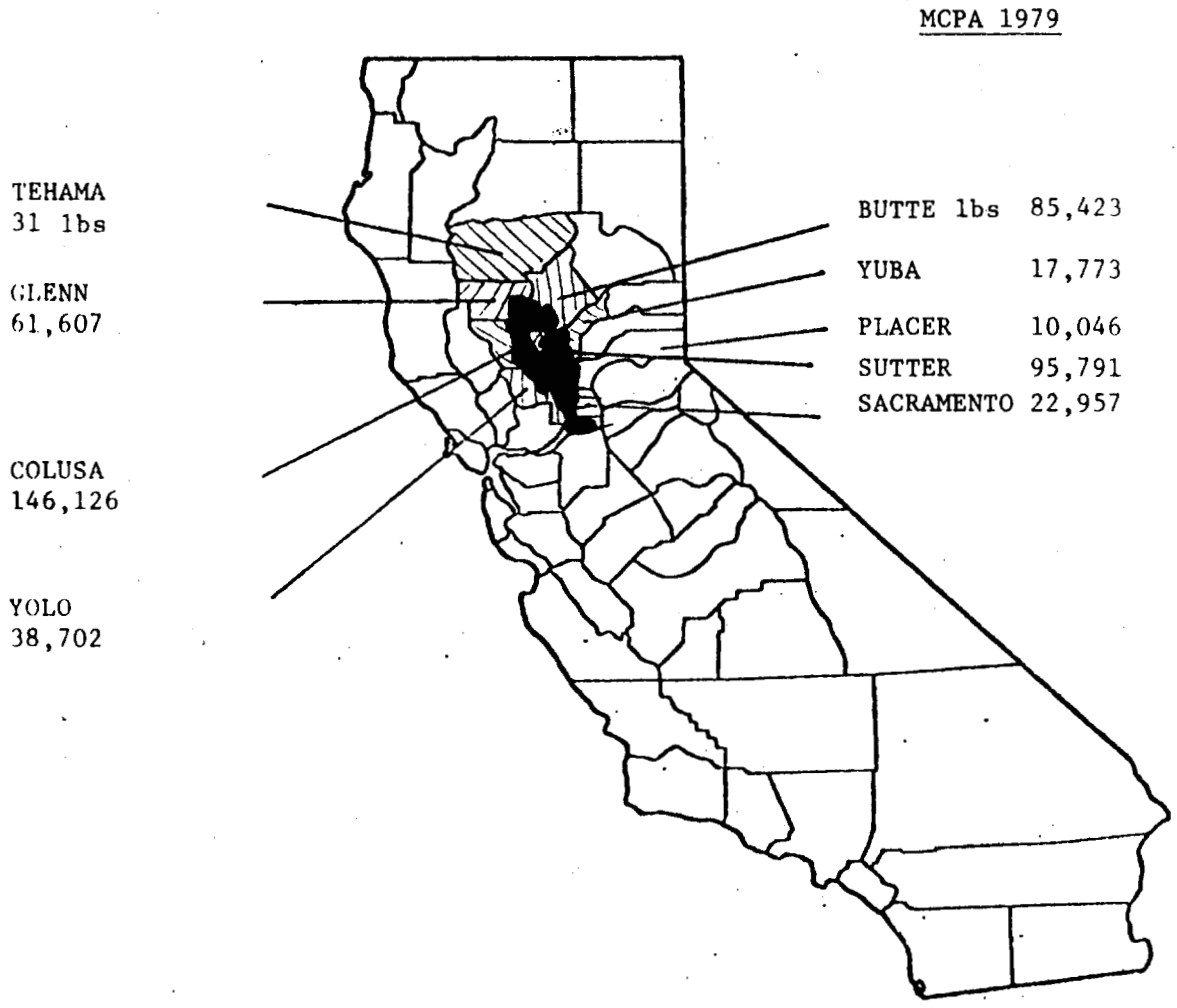

Fig. 1. MCPA applications in 8 counties, 1979.

Heavy shading indicates major use areas

(See Appendix III).

III. THE COMPOSITION AND CHEMICAL REACTIONS OF MCPA SPRAY

Since 1951, MCPA (4-chloro-2-methylphenoxyacetic acid) has been applied for weed control in California rice fields. In 1979, 80% of the state's half-million acres of rice were sprayed with the herbicide, primarily as the dimethylamine (DMA) salt. Earlier work (Soderquist and Crosby, 1975) demonstrated that a significant proportion of the aerially-applied spray did not reach its intended target, and concern over the environmental fate of possible spray drift prompted the present project.

The objectives of our work were (1) to determine the original composition and physical characteristics of MCPA/DMA concentrate and spray and (2) to investigate changes in the spray composition due to evaporation, photodegradation, and other environmental factors.

MATERIALS AND METHODS

"MCP Amine" concentrate (Dow Chemical Co.) was that used to mix spray in the field. The label states that it contains 4 lbs/gal. MCPA acid equivalent as the dimethylamine salt (52.1%, or 589 g/L, of the salt). Spray was prepared by dilution of this aqueous concentrate with about 40 volumes of water (final concentration 14.7 g/L, 0.06 M).

Reagents and solvents were the purest grade available commercially. Pure MCPA was prepared by acidification of the DMA formulation and repeated recrystallization of the precipitated acid from benzene, mp 119-120°. Other phenoxyacetic acid standards were purchased or were prepared from the corresponding pure phenols by reaction with ethyl bromoacetate and subsequent hydrolysis (Synerholm and Zimmerman, 1945). Ethereal diazomethane was prepared by the standard procedure (de Boer and Backer, 1963).

Dimethylamine (DMA) salts were prepared by bubbling excess gaseous dimethylamine into a benzene solution of the acid at room temperature and subsequent evaporation of solvent. The MCPA salt (I) was difficult to crystallize, mp 60-61°, and CHN analysis indicated it was impure. Preparation from acid and amine in ether provided purer material, mp 94-95°. The salts were soluble in chloroform, dichloromethane, acetonitrile, or alcohols but insoluble in ether, benzene, or acetone.

4-Methoxy-2-methylphenoxyacetic acid (V, R=H) was prepared by diazotization of 4-methoxy-2-methylaniline (Aldrich Chemical Co.) and hydrolysis of the resulting diazonium salt with hot dilute acid (Adams et al., 1972) to 4-methoxy-2-methylphenol. The phenol was converted without further purification into the desired product by reaction with ethyl bromoacetate and subsequent hydrolysis (Synerholm and Zimmerman, 1945). Recrystallization from benzene gave white crystals, mp 118.9-119.4°.

Mass spectrum: m/e 196 (M^+), methyl ester m/e 210 (M^+). NMR spectrum: δ2.28 ($PhCH_3$), 3.76 (OCH_3), 6.7-6.8 (Ph-H) ppm.

4-Chloro-2-methylphenoxy-N,N-dimethylacetamide (VIII) was prepared by boiling MCPA with excess thionyl chloride, evaporation, and reaction of the resulting acid chloride with excess dimethylamine in benzene. The product was recrystallized from iso-octane, mp 43.5-44.5°.

Mass spectrum: m/e 227 (M^+), 192 (M-Cl), 155 ($M-CONMe_2$), 72 ($CONMe_2$ base). Ir spectrum: 6.20μ (amide C=O).

4-Chloro-2-methylphenyl formate (II) was prepared by treating the phenol with a mixture of acetic anhydride and formic acid (1:1 v/v) containing a trace of sodium formate as a catalyst (Van Es and Stevens, 1965). The

material was recrystallized from carbon tetlachloride but apparently was contaminated with the parent phenol.

Mass spectrum: m/e 170 (M^+), 142 (M-CO) 107 (M-COCl, base). The formate was not stable and decomposed to its phenol after several days.

Formulation Analysis. Formulation samples were made strongly acidic, extracted with chloroform or dichloromethane, and the extractives remaining after evaporation of the ether were methylated with ethereal diazomethane. Neutral constituents were isolated by continuous extraction of the highly basic formulation with benzene. The products were analyzed by gas chromatography (GLC) on a Varian Model 1740 instrument fitted with a flame ionization detector and either a 150 x 0.21 cm column of 5% OV-17 on Chromosorb G or a 300 x 0.21 cm column of 10% DC-200 on Gas Chrom Q. Nitrogen carrier gas was used at 30 mL/min with the shorter column and 20 mL/min with the longer one. GLC with mass spectrometric detection (GCMS) was conducted with a Finnigan Model 3000 Peak Identifier equipped with a 120 x 0.3 cm glass column containing 2% OV-1 on 60/80 mesh chromasrob G.

Alternatively, formulations and degradation products were analyzed by high-pressure liquid chromatography (HPLC) on a Waters Associates Model 440 instrument fitted with a 254 nm ultraviolet (UV) detector and a Partisil ODS 10 Reverse Phase C_{18} column. The preferred solvent system was 50% aqueous methanol or 15% aqueous acetonitrile containing phosphate buffer (pH 2.83) which permitted direct injection of the formulation.

Photodegradation. Thin films or small droplets of MCPA/DMA spray were placed on the bottom of 20 x 20 cm borosilicate glass dishes and exposed to summer sunlight in Davis, California, or held in the dark as controls.

Alternatively, aqueous spray was irradiated with an F40BL fluorescent UV lamp in a laboratory photoreactor (Crosby and Tang, 1969) or as thin films under F40BL lamps. Irradiated films were dissolved in methanol, or the irradiated solutions were extracted with ether, and the organic extracts were analyzed by GLC.

Trapping of volatile photolysis products was accomplished by irradiating a thin film of spray on the walls of a borosilicate glass flask through which a slow tream of purified air was flowing. Volatile products were removed from the exit air by passing it through 0.1 M aqueous sodium hydroxide solution protected from light; at predetermined times, the alkaline solution was removed, acidified, extracted with methylene chloride, and the extractives analyzed by GLC. Volatilization of dimethylamine was measured by bubbling purified air through spray solutions, trapping any evolved amine in dilute acid, and weighing the solid trap residues remaining after evaporation.

Field Applications. MCPA/DMA concentrate was diluted with about 40 volumes of water and applied as spray from fixed-wing aircraft to two commercial rice fields in Butte Co., California. Air temperature was approximately 25°C and wind speed 1-8 mph (0.5-3.7 m/sec) at the time of application. Field A was calculated to receive 12 oz/acre (840 g/ha) of MCPA acid equivalent, and Field B 14 oz/acre (980 g/ha), from an altitude of approximately 3 m.

Glass dishes were set out, 15 m apart, in each field for 300 m across the path of application. During a period of hours after spraying, the dishes were collected, rinsed, and the amount of MCPA determined by GLC analysis.

RESULTS AND DISCUSSION

MCPA Formulation. MCPA/DMA formulations appear as brown homogeneous solutions, almost odorless, with a pH of 8.0-8.1. Droplets (10 µL) of 40:1 aqueous spray on a glass surface evaporated to sticky, viscous spots rather than to crystalline deposits, and although a thin layer (~0.025 mm) of spray also evaporated rapidly during the first hour (Fig. 2), the loss of water was never complete. Unlike the DMA salt of 2,4-D, the MCPA salt was soluble in nonpolar solvents such as benzene or ether, crystallized only with difficulty, and even then represented an impure substance of variable composition.

At least 18 impurities have been reported to occur in technical MCPA (Sjoberg, 1950; Freeman and Gardner, 1953; Haddock et al., 1959; Gardner and Overton, 1960; Stevens and Grorud 1979) due principally to the impure o-cresol and 4-chloro-o-cresol used in earlier periods of manufacture. As confirmed by GLC, HPLC, and GCMS, the MCPA/DMA applied to California rice in 1979 was of much higher purity (Table 4, Fig. 3A), perhaps indicating a change in manufacturing process. 2-Methylphenoxyacetic acid was the principal impurity (1.0%), together with smaller amounts of 6-chloro- and 4,6-dichloro-2-methylphenoxyacetic acid and traces of other substances.

Neutral extractives were almost entirely absent at levels above a few ppm of the MCPA. The amide IX was present at about 300 ppm, apparently formed by slow reaction of acid and amine even in dilute aqueous solution (Morawetz and Otaki, 1963). Huston (1972) reported three bis(dichlorophenoxy) methanes to be the principal neutral contaminants of production-grade 2,4-D (2,4-dichlorophenoxyacetic acid); if the corresponding 4-chloro-2-methyl-phenol derivatives were present in MCPA, they were below the present levels of detection, and other neutrals such as chlorodioxins also remained undetected.

Photochemical Degradation. Previous work (Soderquist and Crosby, 1975) indicated that MCPA was photochemically degraded with a half-life of about 18 days in a 1.0 mg/L (5×10^{-6} M) aqueous solution at pH 8.3. However, when droplets of MCPA/DMA spray (14.7 g/L, 0.06 M) on a glass surface were exposed to sunlight, 60% of the MCPA had disappeared within one work-day (about 8 hrs irradiation), and less than 20% remained after 3 days; dark controls at about the same temperature remained almost unchanged (Fig. 4).

Analysis of the residues by GLC or GCMS revealed several changes (Fig. 3B): a large increase in the proportion of 4-chloro-o-cresol (IV), a decline in the level of 2-methylphenoxyacetic acid (II), and the presence of p-chlorophenoxyacetic acid (VII) and two unknowns, A (m/e 227) and B (m/e 152), not observed in the dark control (Fig. 3A). The amount of unknown B was very small; the mass spectrum showed it to contain one Cl, and the only reasonable formula appeared to be C_8H_5OCl (Beynon and Williams, 1963) corresponding to a monochlorobenzofuran possibly derived by self-condensation of 4-chloro-2-formylphenoxyacetic acid and dicarboxylation of the resulting coumarilic acid.

Within several minutes after the onset of irradiation, the odor of 4-chloro-o-cresol (IV) became noticable. Analysis of acidic volatiles trapped during photolysis experiments showed IV to be the principal constituent, along with smaller amounts of o-cresol and p-chlorophenol presumably derived from II and VII, respectively (Crosby and Wong, 1973). Also trapped was a substance, m/e 170, whose properties were identical to those of synthesized 4-chloro-2-methylphenyl formate (III), the expected intermediate in phenoxyacetic acid photolysis (Crosby and Wong, 1973). Sunlight irradiation of aqueous IV in a flask sealed to prevent volatilization resulted in a

photolysis rate almost equal to that of MCPA/DMA and an outdoor half-life of 2.5 days (Fig. 5). HPLC analysis showed the presence of many photolysis products, including 2-methyl-p-benzoquinone (V) and a large, highly polar polycarboxylic acid fraction at short retention times. The generation of these acids is reflected in the steady lowering of pH which parallels the photolysis of both MCPA and IV (Fig. 4).

Our previous work (Crosby and Wong, 1973) also led us to expect photonucleophilic displacement of the MCPA ring chlorine by hydroxyl and GLC detection of the 4-hydroxy-2-methylphenoxyacetic acid (VI,R=H) as its methylated derivative. A standard of the acid was synthesized, but repeated attempts to detect it in photolysis mixtures were unsuccessful. However, the detection of the p-benzoquinone from photolysis of IV strongly suggests that loss of the acetic acid sidechain occurs much more rapidly than chloride replacement.

The m/e 227 of unknown A corresponded to a formula of $C_{11}H_{14}ClNO_2$, and the compound proved identical chromatographically and spectrometrically to a synthesized standard of 4-chloro-2-methylphenoxy-N,N-dimethylacetamide (IX). Upon reexamination, the original MCPA/DMA concentrate was found to contain 300 mg/L of IX, and a commercial formulation of 2,4-D/DMA likewise contained its corresponding amide (Table 5). However, sunlight exposure of either the formulations or pure amides on dishes resulted in increased amide formation (Table 5); although the formation of amides from amine salts in aqueous solution has been described and explained (Morawitz and Otaki, 1963), and the thermal reaction is well known (Que Hee and Sutherland, 1974), the photochemical conversion has not been described previously. Exposed to

sunlight, IX itself decomposed with a half-life of 3.5 days (Fig. 6), but the observed photoproducts were not identified; dark control levels also diminished by about 15%, perhaps due to slow volatilization.

The observed photodegradation products are rationalized as shown in Fig. 7. The intermediates in MCPA demethylation to VII and the oxidation of the aromatic ring to aliphatic acids remain unknown.

Volatilization. When air was passed over the irradiated formulation, the chlorocresol IV was quantitatively removed by volatilization as it formed. Likewise, the other phenols and the formate ester (III) volatilized readily. MCPA/DMA has been reported to have an extremely low volatility from its formulation (Grover, 1976); in fact, it is likely that the salt is essentially nonvolatile and that the detected MCPA resulted from its hydrolysis. While the trap contents in our experiments yielded a variety of volatile photoproducts, neither MCPA nor the amide IX were apparent.

Fate of Airborne MCPA/DMA. Analysis of the dishes collected after MCPA/DMA spray application indicated that in Field A, presumed to be treated with 12 oz/acre (0.84 kg/ha) as MCPA, only 0.36 kg/ha (43%) could be accounted for; in Field B, receiving 14 oz/acre (0.98 kg/ha), only 0.24 kg/ha (24%) was found. Although such sampling is open to a number of errors--for example, photodegradation in dishes awaiting collection and the lack of accurate sprayer calibration--the results suggest that a significant proportion of small droplets may indeed remain for some time in the atmosphere.

Although no laboratory degradation studies were made on actual spray droplets, the results of the experiments with bulk spray and spray residues allow at least a qualitative picture of atmospheric fate to develop. Airborne

droplets evaporate quite rapidly to give sticky, highly concentrated particles which would continue to undergo photochemical degradation with continual loss of volatile products such as III, IV, VIII, and o-cresol. Other volatile photoproducts, such as the dimethylamide IX and p-benzoquinone (V), also might be released but at much slower rates due to their slower formation. Within a week, should the particles drift that long, the atmospheric degradation would be largely complete, and the terminal residue from MCPA/DMA application should consist primarily of nonvolatile organic acids and their dimethylamine salts.

To test this conception, high-volume air sampling during and after field application of MCPA/DMA (Woodrow et al., 1980; This Report, Section IV) demonstrated the presence of MCPA and increasing proportion of 4-chloro-o-cresol in the atmosphere; although there also was evidence of p-chlorophenol, no dimethylamide was detected (next section).

ACKNOWLEDGEMENTS

We gratefully acknowledge the technical contributions of K.P. Downes, C.L. Reece, J.N. Seiber, and J.E. Woodrow. The research was supported, in part, by the California Department of Food and Agriculture (Agreement 7458), The California Rice Research Foundation, and U.S.D.A. Regional Research Project W-45.

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Table 4. Analysis of MCP-Amine Formulation

Constituent	Amount (%)	Method
Phenoxyacetates		
4-Chloro-2-methyl-	>95	GLC, HPLC, GCMS
2-methyl-	1	HPLC, GCMS
6-Chloro-2-methyl-	0.5	GCMS
4,6-Dichloro-2-methyl-	0.5	GCMS
Other Dichloro-2-methyl-	trace	GCMS
Phenols		
4-Chloro-2-methyl	>0.5	GLC
4,6-Dichloro-2-methyl-	trace	GCMS
Neutrals		
4-Chloro-2-methylphenoxy-*N*,*N*-dimethylacetamide	0.03	GLC

Table 5. Photochemical Generation of Dimethylamides

Source	N,N-Dimethylamide (ppm)	
	Dark	Light (5 days)
MCPA Formulation	391	1375
Pure MCPA/DMA	0	350
2,4-D Formulation	317	14,000
Pure 2,4-D/DMA	0	300
Pure 2,4,5-T/DMA	0	250

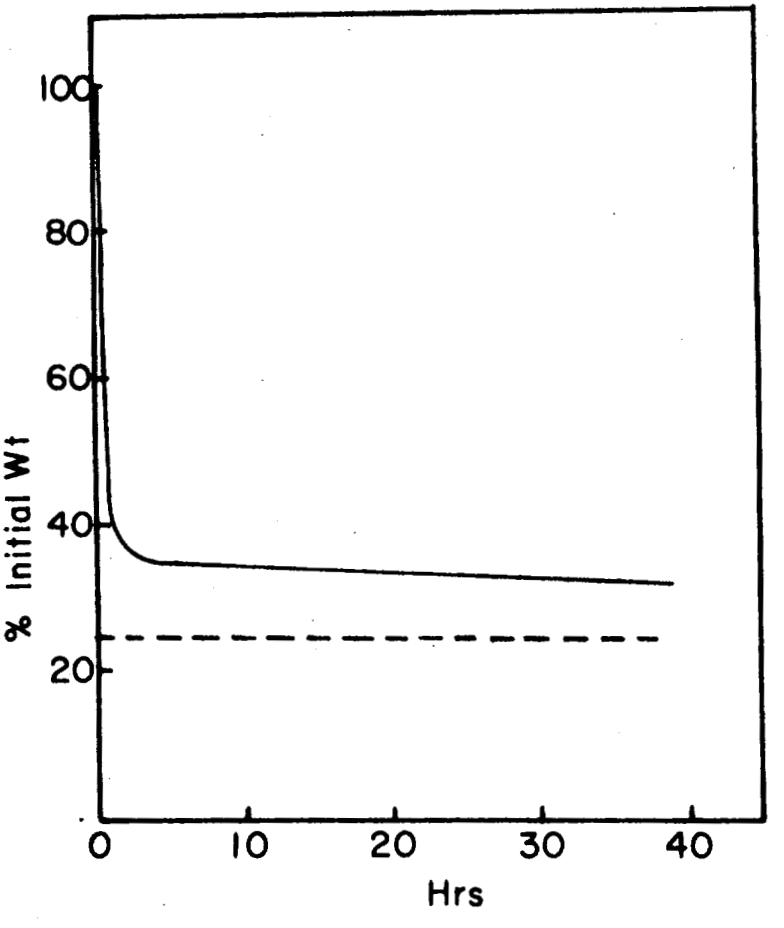

Fig. 2. Evaporation rate of MCPA spray on a glass surface. Dashed line corresponds to complete loss of water.

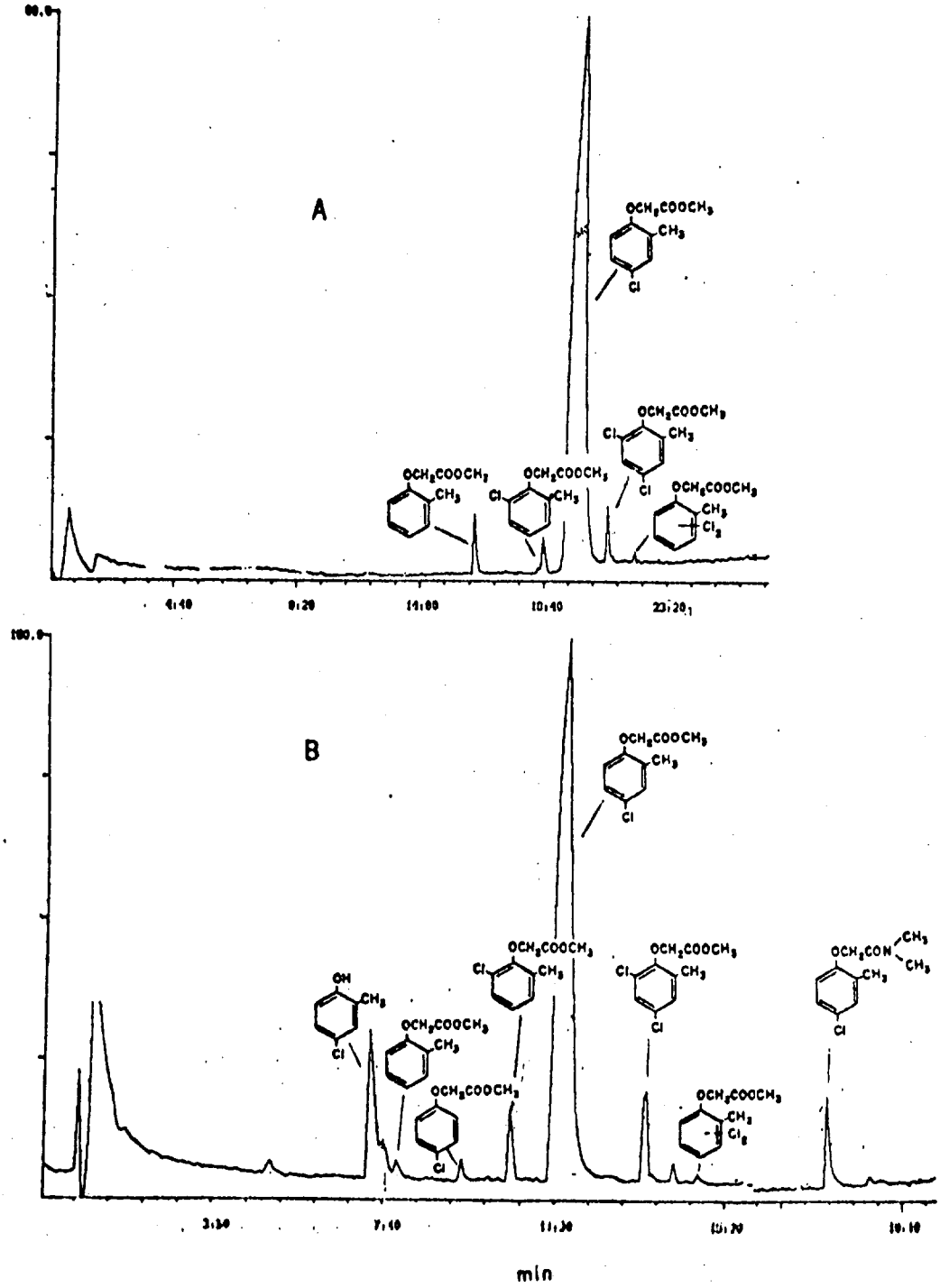

Fig. 3. GC-MS of "MCPA Amine" constituents (methylated), (A) before and (B) after 6 days (40 hrs) of sunlight irradiation.

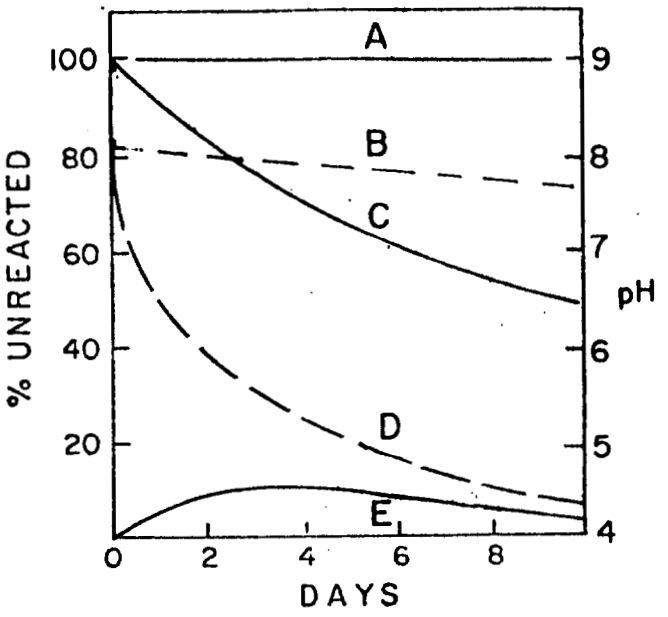

Fig. 4. Photodegradation of MCPA/DMA in sunlight, initial concentration 15 mg/L. A=dark control B=pH control, C=MCPA, D=pH, E=chlorocresol.

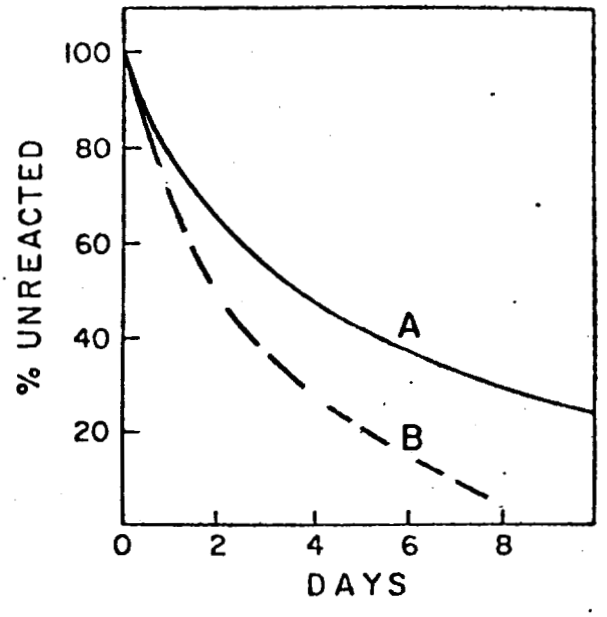

Fig. 5. Photodegradation of chlorocresol in sunlight, initial concentration 200 mg/L. A=chlorocresol B=MCPA.

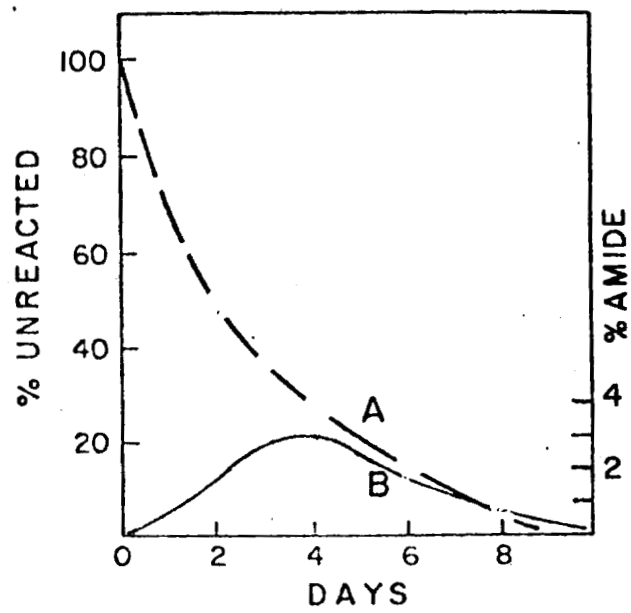

Fig. 6. Formation and photodegradation of MCPA dimethylamide, in sunlight, initial concentration 15 mg/L. A=MCPA, B=amide (right-hand scale).

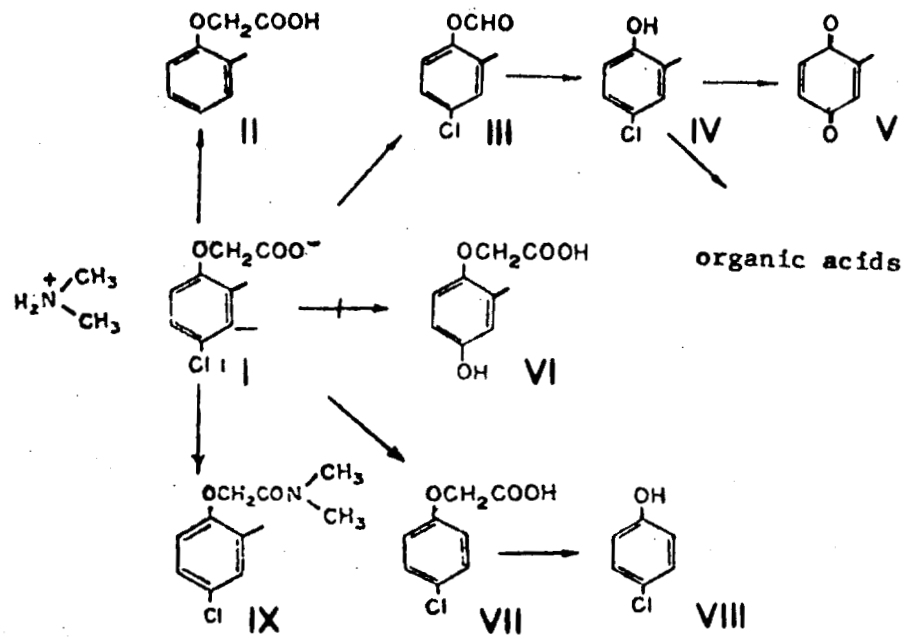

Fig. 7. Photolysis products of MCPA/DMA.

IV. AIRBORNE RESIDUES OF MCPA AND 4-CHLORO-O-CRESOL SURROUNDING TREATMENTS OF MCPA TO RICE--BUTTE COUNTY, 1979

Introduction

The drift of pesticide spray to non-target areas is of concern because of the possible damage that may occur. At best, drift may only be minimized--through the use of specially designed equipment, by the addition of drift control agents to the spray tank mix, and by spraying under optimum weather conditions (i.e., low temperature, low windspeed, and when the wind is moving away from a non-target area) (Akesson et al., 1977; Lawson and Uk, 1979).

A potentially important drift problem is related to the widespread use of the herbicide MCPA in rice culture in Butte County, California. Since many rice fields are located near extensive almond and walnut orchards, there is concern that even a small amount of drift of MCPA into the orchards may adversely affect the trees. We report here the results of a study which was intended to describe the extent of drift of MCPA during application and the movement of airborne residues post-application in defined rice field-adjacent orchard locations. However, no conclusions are drawn concerning the impact of residues in orchard air on the health of the trees because there is presently no basis for correlating airborne residue levels with injury.

Experimental

Field Treatments. Three rice fields, located in Butte County, California, were treated commercially one time each with the dimethylamine salt of 4-chloro-2-methyl phenoxyacetic acid (MCPA) on June 17, 22, and 30 (Figure 1) at 0600-0730, 0817-0945, and 1008-1150, respectively. The rates of application of active ingredient were 1.03 kg/ha (June 17 (65 ha); Rhodia) and 0.84 kg/ha (June 22 (90 ha) and 30 (250 ha); Dow). The June 17 application also included 0.08 kg/ha Nalco-trol^{R} drift control agent in treatments made from the northern boundary of the field to 305 m south of this boundary. The applications were made by fixed-wing aircraft in an east-west direction at an altitude of 3 m above the rice. For the most part, the wind was out of the northwest; windspeed and direction were recorded by a portable weather station near the fields.

Air Sampling. High volume (Hivol) air samplers (Staplex), capable of flow rates greater than 1 m^3/min, were charged with 100 ml 20-50 mesh XAD-4 cross-linked polystyrene macro-reticular adsorbent (Rohm and Haas); the adsorbent was prepared by washing with water and acetone, and then Soxhlet extraction with methanol (1 day) followed with diethyl ether (1 day) with subsequent drying at 50°C in a vacuum oven overnight. The Hivol samplers were placed at various distances up to 1.9 km downwind and adjacent to and inside orchards upwind of the applications (Figure 1). The June 17 application was not monitored; however, air samples were taken approximately one hour, two hours, five hours, one day, and two days post-application. For the June 22 treatment, samples were taken during application, one hour, five hours, one day, and three days after application; air samples were also taken during the June 30 application and approximately 0.5-1 hour afterwards. Two Hivol ambient sampling stations were set up near the two

fields treated on June 22 and 30 (Skinner property shop, North Station) and at the Rice Experimental Station, Biggs, California, approximately 18 km southeast (South Station) (Figures 8 and 9). The samples were operated by electric timers from 0500 to 1600 hours each day from about June 10 to August 3, 1979. In most cases, the XAD-4 adsorbent was changed each day. All air samples were stored in screw-cap jars, transported to Davis, California, and stored at -10°C until analyzed.

Sample Preparation (Figure 10). To each adsorbent sample was added 150 ml Nanograde methanol (MeOH; Mallinckrodt); the samples were swirled on a rotary shaker for two hours, and then were decanted and filtered. The filtrates were reduced in volume to about 10 to 20 ml using a rotary evaporator, diluted with a 100 ml mixture of 0.1 N aqueous sulfuric acid and 5% sodium sulfate in a separatory funnel, and shaken vigorously for about 90 sec with 40 ml Nanograde methylene chloride ($MeCl_2$) with frequent venting. After separation, the $MeCl_2$ layer was drained into a 50 ml centrifuge tube, reduced in volume to 1 to 2 ml under a stream of dry nitrogen and in a water bath heated to 50°C, and then mixed with 1 to 2 ml ethereal diazomethane (CH_2N_2) at room temperature for 30 min. After this time, 2 ml Nanograde hexane was added, excess diazomethane was evaporated under a stream of dry nitrogen using the heated water bath, and the mixture (3-4 ml) was transferred to a hematocrit and reduced in volume to 0.5 ml for gas chromatography (GC). When further cleanup was required, the methylated sample was taken just to dryness and then dissolved in 5 ml benzene. The solution was added to the top of a 7 cm x 1.6 cm column of 80-100 mesh PR grade Florisil (activated overnight at 110°C in a drying oven) prewashed with 35 ml benzene; the addition was followed by 2 x 5 ml benzene washes of the hematocrit. The Florisil column was then eluted with 40 ml 6% diethyl ether in benzene and the eluate was adjusted in volume for GC.

Gas Chromatography. GC was accomplished using a Dohrmann gas chromatograph equipped with a Model C-200 microcoulometer, a Model P-100 furnace control, and a 1.5 m x 6 mm (OD) glass column packed with 10% DC-200 on 80-100 mesh Gas Chrom Q at 150°C. After each injection the solvent was allowed to vent to the atmosphere for about 30 sec after passing through the GC column. The vent was then closed allowing the chromatographed residues to pass to the detector. The minimum detectability, based on detector response to standard injections, was about 3 ng/m^3 for a one hour Hivol sample and <1 ng/m^3 for an ambient Hivol sample. The samples were quantitated by comparing peak heights with those of standards of MCPA and 4-chloro-o-cresol (4-CLOC), a major breakdown product of MCPA (Figure 11). Confirmation of MCPA and 4-CLOC in some of the air samples (four out of over 100) was accomplished using a Finnigan Model 3200 gas chromatograph/mass spectrometer (GC/MS) equipped with a Model 6000 data system. The GC oven contained a 15:1 splitter and a 30 m glass capillary column coated with SP2250 (Supelco) which was programmed from 100°C to 240°C at 8°C/min. At 3 sec/scan, a typical run time for each sample was about 15-20 min. The mass spectral data are as follows (Figure 12): For MCPA (methylated)-m/e 214 (parent), m/e 141 (base), m/e 155, m/e 89 (tropylium cation), and m/e 77. Associated with each fragment (except m/e 77 and m/e 89) was a fragment containing the ^{37}Cl isomer ($^{37}Cl/^{35}Cl = 0.333$); for 4-CLOC (not methylated)-m/e 142 (parent), m/e 107 (base), m/e 89 (tropylium cation), and m/e 77. Associated with m/e 142 was the ^{37}Cl isomer fragment m/e 144 (144/142 = 0.333).

RESULTS AND DISCUSSION

Sampling and Analysis. XAD-4 resin has proved to be an efficient trapping agent for a variety of pesticides (Woodrow and Seiber, 1978; Seiber et al., 1980).

When MCPA was spiked in known amounts to XAD-4 and air was drawn through the mixture using a Hivol sampler operated at ca 1 m^3/min for 90-120 min, recoveries of MCPA were in excess of 80%. This high recovery partly reflects the low volatility of the amine salt of MCPA (estimated vapor pressure of ca 10^{-10} mm Hg, by analogy with that of the amine salt of 2,4-D reported by Hee and Sutherland, 1974) rendering it immobile in the resin bed, and the good solubility of the salt in the methanol extracting solvent. By contrast, the recovery of 4-CLOC spiked as vapor to the resin bed in a similar test was 44.8 ± 2.4% (average and one standard deviation of three replicates); this apparently reflects the higher volatility of 4-CLOC when compared with MCPA amine salt, since the extraction of resin spiked with 4-CLOC but not subjected to an air flow gave recoveries in excess of 80%.

Under actual spray conditions, the amounts of MCPA amine salt existing as vapor should be very low and air sampling, then, would involve trapping essentially only aerosols; however, the trapping efficiency of XAD-4 for aerosols is not known. In an earlier study using polyurethane foam to trap airborne dust, poor trapping efficiencies were observed (Adams and Caro, 1978). However, the aerosols of MCPA formulation resulting from the evaporation of larger aqueous aerosols would be "sticky" drops of liquid rather than dry crystalline material. This may aid XAD-4 in trapping the material from air. The ability of XAD-4 to trap aerosols from air is presently under investigation.

The methanolic extracts of XAD-4 air samples contained residues of MCPA amine salt, 4-CLOC, and potentially the MCPA free acid. Dilution with 0.1 N sulfuric acid converted the amine salt to the acid (pK = 3.28) and insured efficient partitioning of MCPA into the $MeCl_2$ phase. Subsequent treatment with diazomethane gave a rapid and quantitative conversion to the volatile methyl ester (confirmed by GC/MS). On the other hand, the phenolic group of 4-CLOC is very

weakly acidic, underscored by the fact that only about 50% of 4-CLOC in a non-polar solvent is extracted into pH 13 aqueous base. Apparently because of this, 4-CLOC was not methylated to any appreciable extent by diazomethane in the time required for complete methylation of MCPA. Based on relative peak height of gas chromatograms, methylated 4-CLOC accounts for only 7 to 8% of the total cresol residue. Thus, 4-CLOC was quantitated as the unmethylated phenol.

Rice Field Air Samples. Prior to the three applications, air samples were taken in the same area to establish background levels of MCPA and 4-CLOC (Table 6). Out of the six samples taken, only two contained measurable MCPA residues (near the detection limit), and none had 4-CLOC residues above the detection limit. It is noteworthy that one of the two samples that contained MCPA was taken at the south edge of an almond orchard (Price orchard, Figure 8). Since no applications had been made in the immediate area, residues occurring at the sampling stations may have been brought in by the prevailing south, southeast winds from applications made much further south.

In the vicinity of the three test fields, the winds blew from the northerly directions infrequently (Table 7) and it was generally during these brief periods (a few hours at most) that MCPA spraying was allowed by the Butte County Agricultural Commissioner. By far the predominate winds in this area were from the south and southeast. This meant that, in practice, one could collect downwind air samples south of a specific field only during spraying and, at best, for a few hours post-spraying. At other sampling times it was difficult to correlate observed airborne residues with specific treatment locations, as any treated fields south of the study area (where rice is the major crop) could have contributed to residues collected by our air samplers.

Replication of results in laboratory tests made of the analytical procedure were quite good. However, we did not have a sufficient number of air samplers to allow for collecting replicates routinely at the same location for rigorously testing variability in the field. At only six field sampling locations of more than 100 employed in the tests to be described below were duplicate samples taken. The agreement for these duplicates (Table 8) was generally satisfactory; expressing the difference between nanograms trapped by two duplicate samplers as a percent of the mean of the two ($\Delta/\bar{x}$ X 100), variabilities for MCPA ranged from 0.6 to 36% (average variability 11.4%) while for 4-CLOC they were from 1.5 to 51% (average variability 29.8%).

The June 17 application (Table 9) was made to a rice field in Section 9 (Johnson; Figure 8) located on the south side of Pratt-Grant road at 0600-0730. A mature almond orchard (Price) was located to the north just across Pratt-Grant road. No air samplers were operated during the spray treatment, but post-spray air samples were collected up to two days following treatment at several sites near and within the field, and 30 m inside the orchard. Low but measurable MCPA residues (3-65 ng/m^3) were obtained in most samples taken at the south edge of the treated field and at distances up to 1.9 km south of the field during the two-day post-spray sampling. Generally, the levels declined with increasing distance from the field such that at the 563 m and 1.9 km south sites at 1 hr, 5 hr, and 1 day post-spraying only one sample of 5 showed a residue (11 ng/m^3) above the approximate detection limit. It should be noted, however, that the wind was predominately from the west and south, southeast during post-spray sampling done at 5 hr and 1 day, minimizing the chance of residue movement through the air to the south sampling sites at those sampling periods.

Generally higher (<2-281 ng/m^3) 4-CLOC residues were observed in similar south samples except those taken at 5 hr post-spray. Excluding these 5 hr

samples, the ratios 4-CLOC/MCPA were 22.3 (1 hr), 13.1, 7.1, and 23.4 ($\bar{x}$ = 14.5, 2 hr), 3.8, 11.4, 9.4, 14.3 and 70.5 ($\bar{x}$ = 21.9, 1 day), and 1.4 and 0.7 ($\bar{x}$ = 1, 2 day). Considering that 4-CLOC is much more volatile than MCPA-dimethylamine salt or MCPA free acid, the results indicate that airborne 4-CLOC originated by volatilization from the rice field of residues deposited in the rice field with the spray formulation (in which it is a minor constituent) or formed from MCPA in the rice field during post-spray weathering.

Only minor MCPA intrusions (<2-15 ng/m^3) were noted within the Price orchard, and slightly higher residues (8-35 ng/m^3) were at the south edge of the orchard facing the rice field in the post-spray samples. The average ratio 4-CLOC/MCPA within the orchard was 17.6, and at the south edge of the orchard it was 11.1. Both are in rough agreement with ratios recorded south of the rice field, and thus indicate post-spray volatilization from the rice field as the source of 4-CLOC.

Conclusions from the June 17 treatment were: (1) Post-spray airborne MCPA levels in air surrounding the treated field were generally low, as predicted from the low volatility of MCPA-dimethylamine salt; (2) Airborne MCPA was, however, detectable in most post-spray samples; (3) airborne levels of 4-CLOC generally exceed MCPA (ie., ratio > 1) in the post-spray samples, reflecting the ability of the more volatile 4-CLOC to evaporate from the treated field after spraying was completed; and (4) some movement of both chemicals occurred toward and within a nearby almond orchard, but in low levels. The latter is reinforced by the presence of detectable residues of MCPA in almond leaf samples taken in the Price orchard by Winterlin's group on June 17 and 18.

The June 22 application was made to a western portion of Section 14 (Skinner; Figure 8) at 0817-0945. Both spray and post-spray samples were collected adjacent to the field, at several locations south of the field, in an

almond-walnut orchard (McClintock's) located ca 400 m north of the field, and a pistachio orchard (Peterson's) located ca 3.3 km north of the field (Table 10). Downwind (south) samples taken during spray contained MCPA at levels of 573 (south edge of rice field), 295 (201 m south), and 62 ng/m^3 (402 m south) for which 4-CLOC/MCPA ratios were 0.21, 0.07, and 0.11, respectively ($\bar{x}$ = 0.13)--a sharp contrast with June 17 post-spray air samples. The post-spray samples taken at 1 and 5 hr showed much lower airborne MCPA residues than recorded during spray, and an increased 4-CLOC/MCPA ratio ($\bar{x}$ = 1.6).

Samples taken at the north edge of the field showed apparent upwind drift of MCPA (207 ng/m^3 MCPA, and a 4-CLOC/MCPA ratio of 0.1) during spraying. Samples taken at the same location after spraying had 6 (1 hr), 10 (5 hr), 36 (1 day), and 5 ng/m^3 (3 days) with 4-CLOC/MCPA ratios of 9.5, <0.2, 0.69, and 4.8 respectively ($\bar{x}$ = 3.8).

Almond-walnut orchard samples showed levels of MCPA at the detection limit during spraying, minor incursions of MCPA (< 2-13 ng/m^3) at 1 hr, 5 hr, 1 day (am), and 3 days post-spraying, and 4-CLOC/MCPA ratios varying over a wide range from < 1-17.3 ($\bar{x}$ = 4.1) during the same sampling times. The levels of MCPA (107 ng/m^3) and 4-CLOC (275 ng/m^3) in the high orchard sample (ie, one taken just above the orchard canopy) on the afternoon of day 1 post-spray were considerably above all other similar samples (confirmed by GC/MS). We tend to ascribe this to drift from an MCPA treatment made other than in Section 14, and note that a June 23 application was recorded in Section 8 (about 2 miles to the west) while still others may have taken place in rice fields to the south during that afternoon period. Since wind direction during the period the anomalously high samples were obtained was from the southeast, the second explanation is favored.
Leaf residues of samples of McClintock orchard walnuts on days 0 (June 22), and 1 (June 23) showed 0.34 and 0.28 ppm, respectively, and by June 29 were still at 0.24 ppm (cf Section V).

There was no measurable airborne MCPA or 4-CLOC in the pistachio orchard in samples collected during or following the June 22 application to Section 14. There was also no measurable leaf residue (< 0.01 ppm) in this orchard in samples collected on June 22 and 23 (Section V).

Several points regarding the June 22 application and accompanying air samples deserve comment: (1) A second rice field only 0.5 mile south of the study field was sprayed with MCPA at virtually the same time as the study field. Thus, airborne levels recorded south of the study field may have included some residue from the 2nd field. (In fact, one air sampler located 0.5 mile south of the study field received a "direct hit" from the 2nd application and thus was not analyzed). (2) The 4-CLOC/MCPA ratios in downwind samples taken during spraying are much lower than in similar post-spray samples. This is in line with the origin of spray-drift 4-CLOC resting with the formulation applied, as opposed to its origin post-spray by the volatilization mechanism referred to previously in this report. (3) MCPA residues of 33-79 ng/m^3 were recorded just above the rice field at 1 day post-spray, and were generally higher in the afternoon than in the morning. This, when combined with similar results from in-field air samples taken at 1 and 2 days post-spray at Section 9 (Table 9), indicate that MCPA itself (logically as the free acid rather than the amine salt) may volatilize from a treated rice field by a similar mechanism to that described for 4-CLOC (but at a lower rate than for 4-CLOC). (4) McClintock orchard air and leaf residues bearing MCPA on days 0 and 1 cannot clearly be ascribed to the Section 14 spraying for, as was noted above, an application was made simultaneously less than a mile south on day 0 (June 22) and at one other rice field west and probably at others further south on day 1 (June 23). Applications further south almost certainly contributed to the anomalously high day 1 afternoon residue in the McClintock orchard since the wind was from the south during that sampling period.

The June 30 application (Table 11) was made to an eastern portion of Section 14 and western portion of Section 13 (Skinner; Figure 8) at 1008-1150. As far as we could determine, this was the only MCPA treatment made that day in the Pratt-Grant road vicinity. Air samples were taken during spraying and 0.5-1 hr post-spraying at locations similarly deployed as in the June 17 and 22 applications, and in two orchards one of which (McClintock's--almonds/walnuts) was located ca 300 m northwest of the north edge of the treated field and the second (Martinez--almonds) ca 804 m north of the treated field. Downwind (south) residues of MCPA declined from 346 ng/m^3 (south edge), to 51 ng/m^3 (201 m south), and to 18 ng/m^3 (402 m south) during spraying. However, 4-CLOC did not show a similar decline with distance (77 ng/m^3 at south edge, 57 ng/m^3 at 201 m south, and 72 ng/m^3 at 402 m south) and the 4-CLOC/MCPA ratios reflected this (0.22, 1.12, and 4.00). In this case, most of the 4-CLOC in air did not originate from the spray drift, but may have come from the field in which the samplers were deployed. This seems likely since the field just south of the June 30 application had been treated with MCPA on June 25 and 27. At 0.5-1 hour post-spray, the same sampler stations had 45, 5, and 12 ng/m^3 MCPA and showed 4-CLOC/MCPA ratios of 2.0, 15.2, and 4.8. The north edge of the field had 46 ng/m^3 MCPA during spray and 10 ng/m^3 0.5-1 hr post spray, with 4-CLOC/MCPA ratios of 1.1 and 5.1, respectively, indicating spray drift and post-spray field vaporization of 4-CLOC.

The northwest orchard (McClintock's) had very low (2 - 11 ng/m^3) MCPA in the spray and post-spray samples but unexpectedly high 4-CLOC residues (144 and 190 ng/m^3) reminiscent of those recorded in the Price orchard on June 17 and 18. A single sample taken in the orchard (Martinez) north of the rice field had 5 ng/m^3 MCPA and 60 ng/m^3 4-CLOC (confirmed by GC/MS). There were no leaf samples taken on this day from either the McClintock or Martinez orchard for comparison with the air residues.

With regard to intrusion of MCPA into nearby orchards, the June 30 application indicated that such intrusions should be very low when wind direction is from orchard to field (as was the case for the McClintock orchard), when the orchard is greater than 804 m upwind or crosswind from the field (the case for the Martinez orchard), and the windspeed is relatively brisk (8 mph in this case) and constant (west and northwest in this case). However, since all of these factors should mitigate against 4-CLOC intrusion as well as MCPA, the finding of high 4-CLOC residues in both orchards is unexplained.

Composite Profiles of Airborne MCPA in the Vicinity of Treated Rice. The downwind (south) dissipation of airborne MCPA for the June 30 application is plotted in Figure 13 using both total volume (TV; Table 11) of air sampled and effective volume (EV). The latter is the product of sampler flow rate and time the wind blew toward the sampler within an arc described by the field dimensions and the sampler position. Total volume, which was used to compute concentrations for all of the samples collected in this study, will not accurately represent airborne residue levels if, under certain spray drift conditions, the wind occasionally shifts away from the samplers so that not all the air sampled contains residues. Using EV, the average concentration of MCPA at each downwind station during spraying was 497 ng/m^3 (south edge), 164 ng/m^3 (201/m south), and 156 ng/m^3 (402 m south). The ratios EV/TV were 1.4 (sough edge), 3.2 (201 m south), and 8.7 (402 m south) indicating that the use of either EV or TV will have a pronounced influence on the assessment of long-distance drift.

Figure 13 shows that rapid decline in concentration occurs near the source followed by a more gradual change with increasing distance; this has been observed for another non-volatile herbicide--paraquat (Byass and Lake, 1977; Seiber and Woodrow, 1980)--and it may be typical of any aircraft sprays containing non-volatile pesticide salts. The dissipation curves suggest (especially the EV

curve) that, depending upon the source strength, measurable residues of MCPA may be found kilometers downwind. However, due to uneven terrain and possible turbulent wind flow, downwind concentrations may be somewhat attenuated.

A composite map of MCPA and 4-CLOC airborne residues based upon the June 22 and June 30 treatments for "upwind" and "downwind" sites both during and just following MCPA application to rice is given in Figure 14. Generalizing, this composite indicates a decline in residue of both MCPA and 4-CLOC with downwind distance during spraying, but that significant downwind drift will extend far beyond 400 m; a rapid decline in airborne residue with time following treatment (approximately by a factor of 10 for MCPA but less for 4-CLOC) at 1 hr post-spray; a lower residue just upwind of the field than just downwind (approximately by a factor of 2-10 for MCPA); very little upwind intrusion of MCPA to orchards beyond 400 m of the field; but surprisingly significant upwind intrusion of 4-CLOC beyond 400 m of the field (a finding which at this point is unexplained).

Ambient Air Samples. The two ambient air sampling stations located on the Skinner property (North Station) and at the Rice Experimental Station (South Station) (Figure 9) gave many samples that contained MCPA and 4-CLOC residues (Tables 12 and 13). Concentrations in air ranged from above 34 ng/m^3 to less than 1 ng/m^3. Generally, the higher values for MCPA were recorded during the period of most intense MCPA use in Butte County during 1979 (June 15-July 1), while for 4-CLOC a trend in this direction was also noted but with greater variability. With regard to the latter, it should be pointed out that recovery efficiencies for 4-CLOC in these ambient samples was likely very low due to the tendency of this chemical to volatilize from the resin during prolonged sampling. This may explain why 4-CLOC/MCPA ratios in these ambient samples were generally much lower than might have been expected from shorter interval samples taken near known application sites.

While long-distance drift from remote applications is a possible contributing source, many of the samples were collected on days when known applications took place in the general area about each station (indicated by + in Table 12). Only one documented application near the South Station is available thus far. It took place on June 22 at the Rice Experimental Station south and west of the sampler and is probably responsible for the enhanced residues observed since the wind was predominately from the west and southwest during that sampling period. Depending upon the meteorological conditions prevalent during the applications, the actual concentrations in the vicinity of the air samplers may have been considerably higher than the time-averaged concentrations would indicate. For example, the June 30 North Station sample was taken 10 to 12 m west and northwest of a known application in Sections 13 and 14. Concentrations of MCPA and 4-CLOC in air based on the time of spraying only were almost six times greater than the time-averaged concentrations. At best, ambient samples give minimum concentrations of airborne residues.

Summary

Aerial application of MCPA in this study led to measurable spray-related residues up to 400 m downwind for both MCPA and 4-CLOC. This implies that measurable residues would occur at even greater distances downwind. Residues were also measured in the orchards north of the treatment sites in spite of the wind limitations prescribed by the Butte County Agricultural Commissioner. However, the effect, if any, of the observed residue levels on the health of the trees is not known. Some of the post-spray air samples seem to indicate that MCPA may be vaporizing along with 4-CLOC from the treated fields. Further insight into this possibility might be gained through vaporization measurements in the laboratory. While MCPA and 4-CLOC residues in the ambient samples no

doubt reflected primarily local applications, long-distance drift from more remote applications must be considered as well. More than 60% of the combined samples from the two ambient stations contained measurable MCPA residues indicating that levels in air probably remain elevated during the spraying season which would allow for widespread distribution. The presence of MCPA and 4-CLOC was confirmed by GC/MS in only four samples out of over 100 taken; any time a sample chromatogram matched the standards, it was assumed that the sample contained MCPA and 4-CLOC.

Acknowledgments

We wish to thank the following for their cooperation in this study: Messrs. C.M. Johnson and E. Skinner who provided the necessary rice fields; the Price Family, Messrs. McClintock, Martinez, and Peterson who granted us permission to sample their orchards; the Rice Experimental Station, Biggs, California (Dr. D. Siemons), for maintaining South Station; P and M Dusters, Durham, California, and AgAv, Richvale, California, who scheduled and made the applications; and Mr. C. Wick, Agricultural Commissioner's Office, Butte County, who acted as liaison between the University of California research group and the rice growers.

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Table 6. Air background samples of a rice field environment, June, 1979

Date	Location	Concentration in Air, ng/m^3[a]	
		MCPA	4-CLOC
6/07	Over untreated rice field	3[b]	<3
6/11	Top of orchard canopy	<3	<3
6/11	1.2 m above orchard floor	<3	<3
6/11	Over untreated rice field	<3	<3
6/11	Over untreated rice field	<3	<3
6/16	At south edge of orchard	4[c]	<3

[a]Calibrated flow of 1.12 m^3/min for about 60 min.

[b]210 ng MCPA

[c]250 ng MCPA

Table 7. Wind direction and average wind speed for the sampling periods.

	Percent of Sampling Time (per 1/4 hr.)								
	N	NE	E	SE	S	SW	W	NW	Average Windspeed, mph (m/sec)
June 17:									
1 hour							45	55	13 (5.8)
2 hours							50	50	9 (4.0)
5 hours						9	64	27	7 (3.1)
1 day		20	10	50	20				3 (1.3)
2 days		50	50						8 (3.6)
June 22:									
Spray		29				43	14	14	1 (0.4)
1 hour						19	81		6 (2.7)
5 hours						45	55		5 (2.2)
1 day a.m.		22	11	67					0.7 (0.3)
p.m.				100					3.0 (1.3)
3 days			29	71					4 (1.8)
June 30:									
Spray							62	38	8 (3.6)
0.5-1 hour						21	68	11	6 (2.7)

Table 8. Variability between duplicate field air samples.

Site	Time	MCPA, ng Rep 1	MCPA, ng Rep 2	MCPA, ng Δ/mean x 100	4-CLOC, n Rep 1	4-CLOC, n Rep 2	4-CLOC, n Δ/mean x 100
S edge	June 22 1 hr	23,100	33,000	36%	14,400	21,900	32%
S edge	June 22 5 hr	17,800	17,900	0.6	6,750	10,800	46
S edge	June 30 Spray	54,400	38,600	17	13,000	7,750	51
S edge	June 30 0.5-1 hr	5,825	5,750	0.6	13,725	8,800	44
402mS	June 30 Spray	2,512	2,600	3.4	10,250	10,100	1.5
402mS	June 30 0.5-1 hr	2,362	1,940	11.0	10,400	10,825	4.0

Table 9. MCPA and 4-chloro-o-cresol (4-CLOC) in air samples taken after the June 17 application.

Station		Concentration in Air, ng/m^3				
		1 hour	2 hours	5 hours	1 day	2 days
High	MCPA	13	--	<2	15	4
Orchard[a]	4-CLOC	183	--	107	183	10
Low		--	--	<2	9	14
Orchard[b]		--	--	78	12	10
South edge		17	--	8	35	6
of orchard		200	--	150	391	15
South edge of		--	13	17	65	16
rice field, 0.3m high[c]		--	170	<2	250	22
South edge of		--	16	8	18	12
rice field, 1.8m high[c]		--	114	<2	206	8
201m south		--	12	3	24	--
of rice field		--	281[d]	24	227	--
563m south		--	--	<2	11	--
of rice field		--	--	<2	157	--
1931m south		3	--	3	<2	--
of rice field		67	--	16	141	--

[a] At the top of the orchard canopy.

[b] ~1.2m above orchard floor next to High Orchard (30 m in from south edge).

[c] Samplers were moved into the treated field on days 1 and 2.

[d] 4-CLOC confirmed by GC/MS.

Table 10. MCPA and 4-chloro-o-cresol (4-CLOC) in air samples taken during and after the June 22 application[a]

Station		Concentration in Air, ng/m^3				
		Spray	1 hour	5 hours	1 day[e]	3 days
High	MCPA	3	<2	<2	13/107	<3
Orchard[b,c]	4-CLOC	3	<2	<2	<2/275	11
Low		3	<2	<2	10	9
Orchard[d]		52	12	<2	12	80
North edge		207	6	10	38/35	5
of rice field		21	57	<2	20/30	24
South edge of		573	137	231	--	--
rice field		122	88	114	--	--
201m south		295	59	69	--	--
of rice field		20	46	101	--	--
402m south		62	5	--	--	--
of rice field		7	24	--	--	--
0.3m above		--	--	--	32/79	10
rice field		--	--	--	44/62	22
1.8 m above		--	--	--	33/59	10
rice field		--	--	--	<2/31	21

[a]Another application took place simultaneously with this one about 804m south of the test field.

[b]At the top of the orchard canopy.

[c]Afternoon MCPA and 4-CLOC confirmed by GC/MS.

[d]~1.2m above orchard floor next to High Orchard (30 m in from south edge).

[e]Morning/Afternoon; other samples were taken during the afternoon.

Table 11. MCPA and 4-chloro-o-cresol (4-CLOC) in air samples taken during and after the June 30 application

		Concentration in Air, ng/m^3	
Station		Spray	0.5-1 hour
NW Orchard	MCPA	<3	--
High[a]	4-CLOC	144	--
NW Orchard		11	2
Low[a]		190	40
North		5	--
Orchard[b]		60	--
North edge of		46	10
rice field		49	51
South edge of		346	45[c]
rice field		77	88[c]
201m south		51[c]	5
of rice field		57[c]	76
402m south		18	12
of rice field		72	57

[a]McClintock orchard: High-at top of orchard canopy; Low-1.2 m above orchard floor next to High; both ~30m into orchard from south edge.

[b]Martinez orchard-south edge.

[c]Estimated concentrations, samplers shut off prematurely.

Table 12. Ambient air samples from North Station

Dates	Sampling Volume, m^3	MCPA Amount, ng	MCPA Conc. in Air, ng/m^3	4-CLOC Amount, ng	4-CLOC Conc. in Air, ng/m^3	Spray[a]	Section Number for Spray
6/13-6/15	1,458	1,980	1	6,000	4	-	-
6/15-6/16	76	7,850	11	2,950	4	+	23, 24
6/16-6/17	1,102	1,325	1	2,800	2	+++	7, 9, 23, 24
6/17-6/18	813	< 200	< 1	< 200	< 1	-	-
6/18-6/19	833	1,660	2	< 200	< 1	-	-
6/20-6/21	806	4,080	5	7,254	9	+	23, 24
6/21-6/23	1,814	6,380	4	< 200	< 1	++++	8, 14, 13, 23, 24
6/23-6/25	1,250	7,650	6	< 200	< 1	++	8, 23, 24
6/26-6/27	759	10,150	13	16,250	21	+	23, 24
6/27-6/29	1,438	5,400	4	9,000	6	-	-
6/29-6/30	766	3,350	4	< 200	< 1	-	-
6/30	638 / 114	10,500	16[b] / 92[b]	12,500	20[b] / 109[b]	+	13, 14
7/1	323	3,360	10	10,910	34	-	-
7/3-7/15	8,622	37,250	4	< 200	< 1	-	-
7/17-8/3	12,513	32,550	3	< 200	< 1	+	12

[a] + indicates number of known applications in general area about the sampling station (up to 5.8 km).

[b] The upper numbers are time-averaged concentrations; the lower numbers are concentrations based on spray time only (1.7 hours; 114 m^3).

Table 13. Ambient air samples from South Station[a]

Date	Amount, ng	Conc. in $_3$ Air, ng/m^3	Date	Amount, ng	Conc. in $_3$ Air, ng/m^3	Date	Amount, ng	Conc. in $_3$ Air, ng/m^3
6/10-MCPA	< 200	< 1	6/19	7,100	10	6/28	3,400	5
6/11 4-CLOC	< 200	< 1		9,600	13		3,925	5
6/11	< 200	< 1	6/20	5,150	7	6/29	3,720	5
	< 200	< 1		12,650	17		2,175	3
6/12	4,150	6	6/21	2,880	4	7/14	2,000	3
	10,000	14		11,350	15		3,000	4
6/13	< 200	< 1	6/22[b]	16,250	22	7/15	< 200	< 1
	< 200	< 1		8,350	11		2,450	3
6/14	9,550	13	6/23	9,750	13	7/16	< 200	< 1
	13,420	18		13,500	18		3,100	4
6/15	< 200	< 1	6/24	4,720	6	7/17	750	1
	< 200	< 1		4,900	7		11,450	15
6/16	7,700	10	6/25	3,900	5	7/18	< 200	< 1
	< 200	< 1		10,050	14		12,200	16
6/17	< 200	< 1	6/26	9,480	13	7/19	385	0.5
	18,000	24		12,200	16		9,950	13
6/18	3,600	5	6/27	8,750	12	7/20	670	1
	10,350	14		13,450	18		2,880	4

Table 13. cont.

Date	Amount, ng	Conc. in Air, ng/m^3	Date	Amount, ng	Conc. in Air, ng/m^3	Date	Amount, ng	Conc. in Air, ng/m^3
7/21	< 200	< 1	7/26	< 200	< 1	7/31	< 200	< 1
	2,090	3		< 200	< 1		2,050	3
7/22	< 200	< 1	7/27	555	0.8	8/1	760	1
	1,580	2		2,350	3		13,225	18
7/23	255	0.4	7/28	610	0.8	8/2	2,450	3
	1,480	2		2,050	3		14,700	20
7/24	< 200	< 1	7/29	850	1	8/3	< 200	< 1
	1,500	2		14,200	19		1,325	2
7/25	1,725	2	7/30	1,525	2			
	2,850	4		11,900	16			

[a]All sampling volumes were 739 m^3, except for the first sample which was 538 m^3.

[b]Application of MCPA took place south and west of sampler.

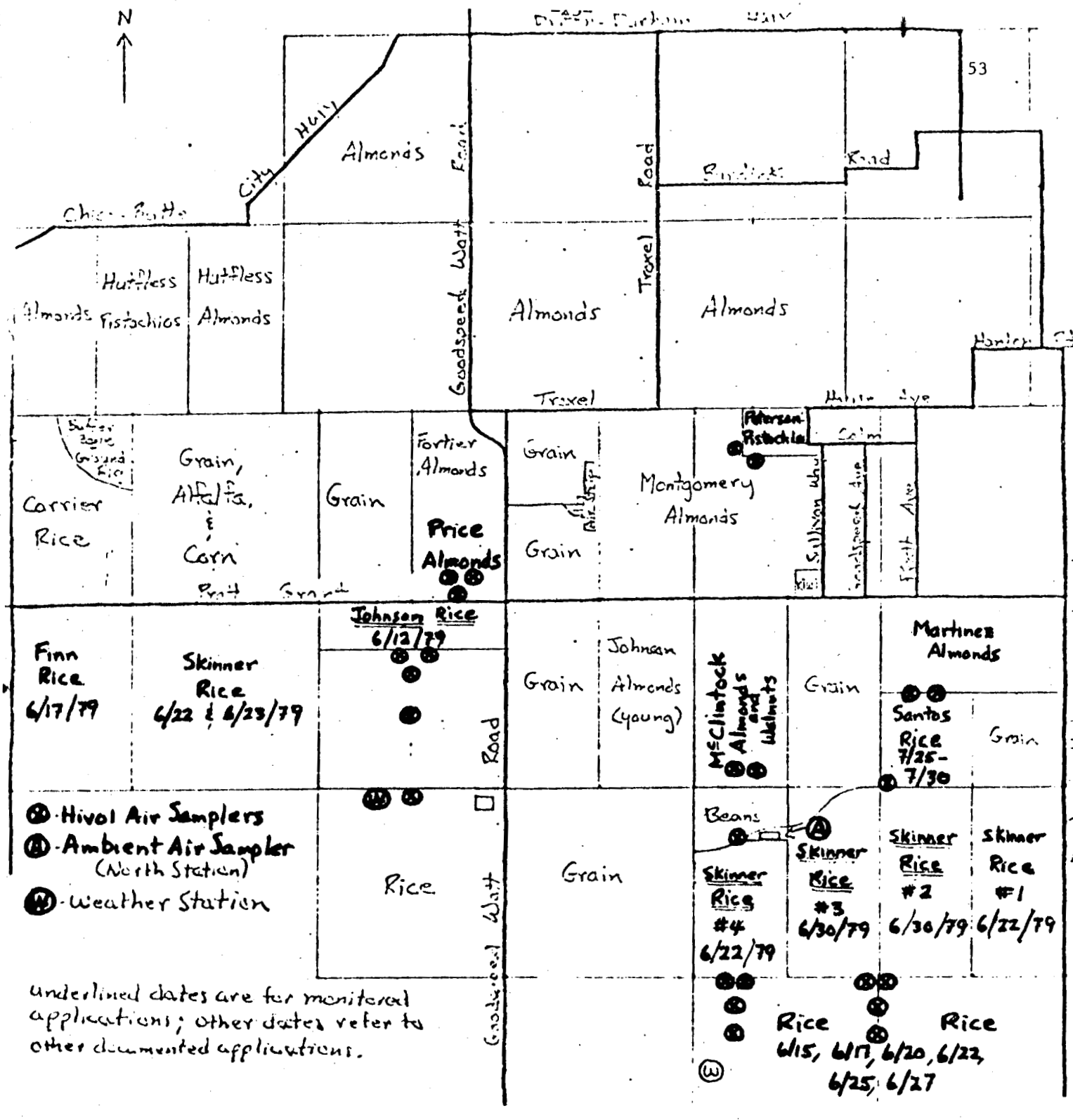

Figure 8. Deployment of Air Samplers for MCPA Applications.

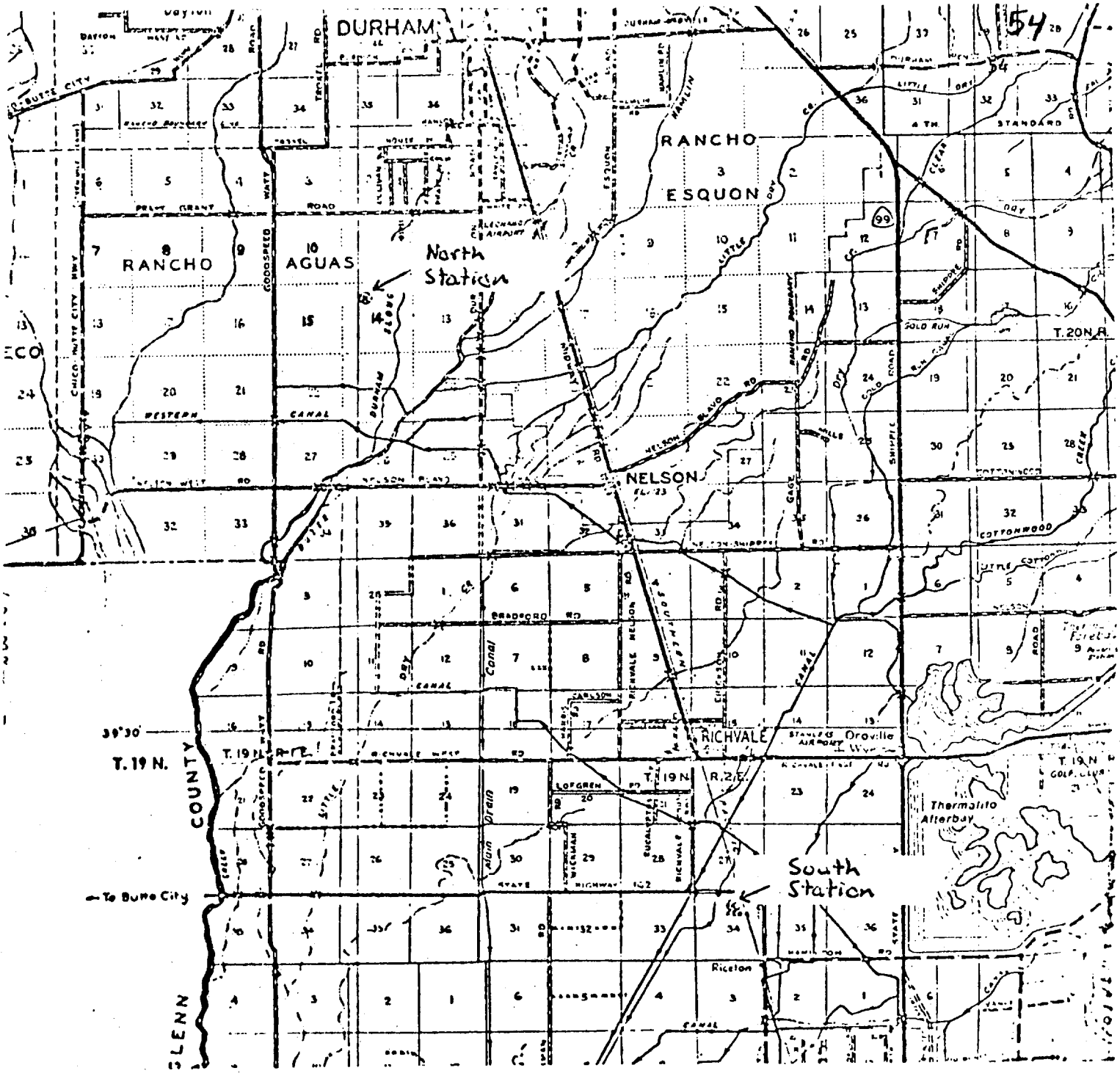

Figure 9. Deployment of Ambient Air Samplers (North Station, South Station).

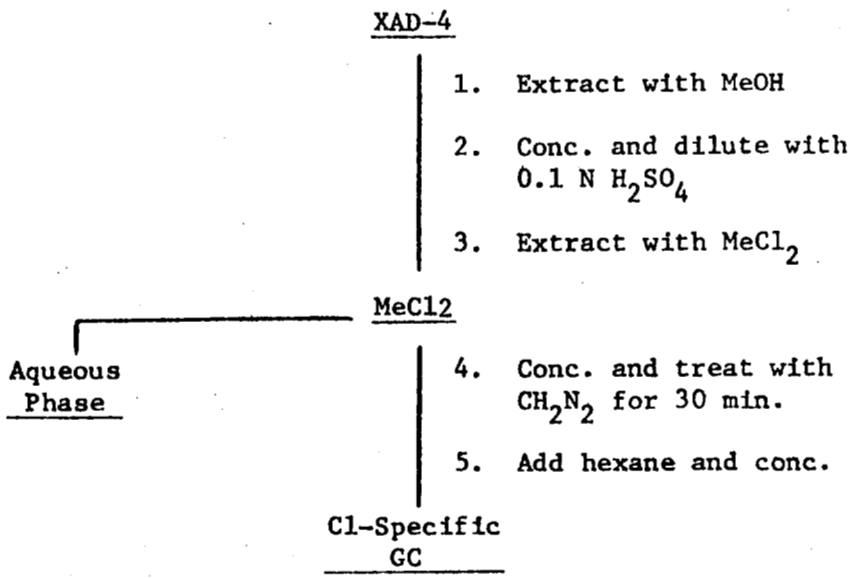

Figure 10. Analytical Scheme for XAD-4 Air Samples Containing MCPA and 4-chloro-o-cresol.

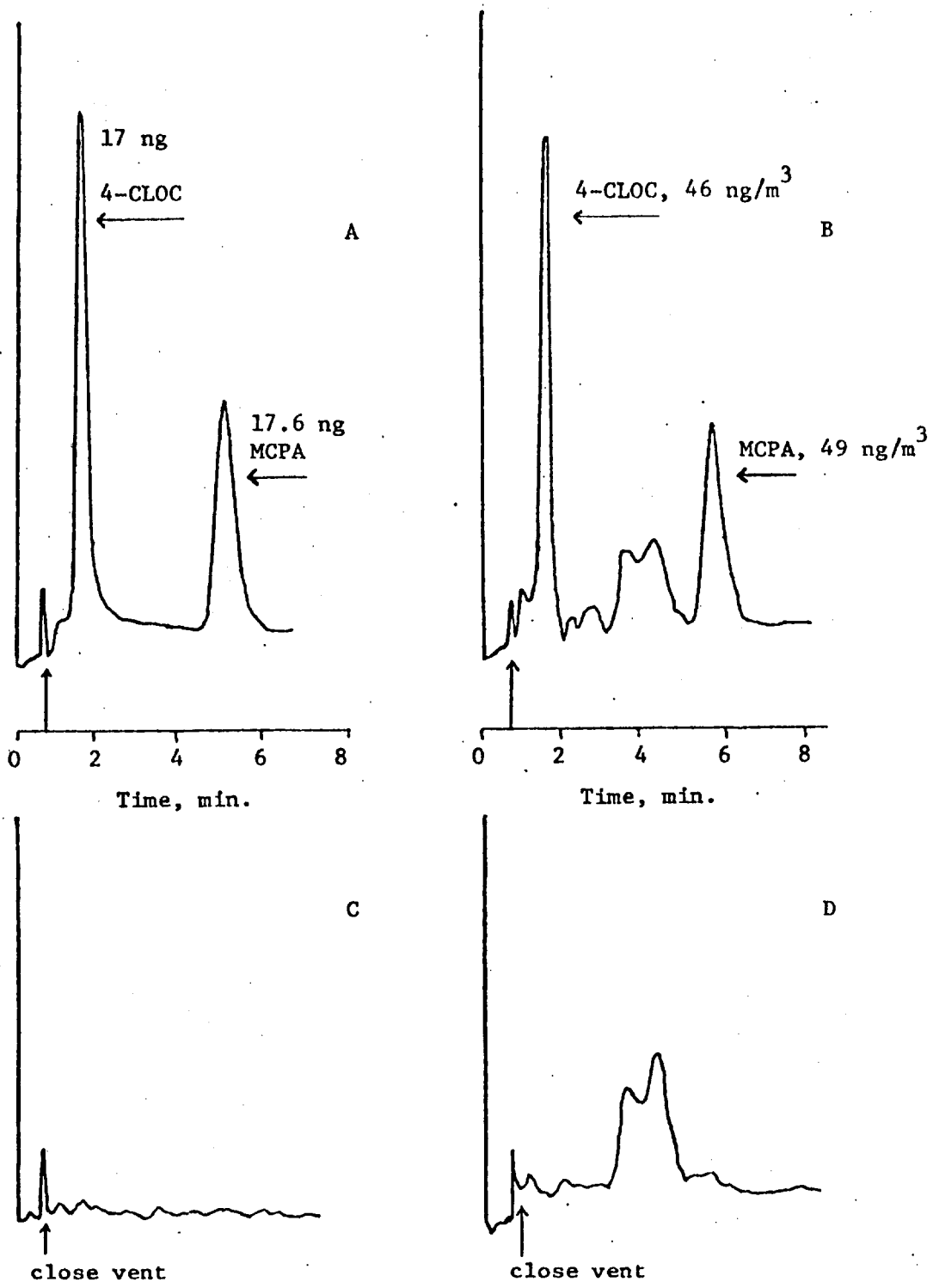

Figure 11. Gas chromatograms of MCPA and 4-chloro-o-cresol (4-CLOC) standards (A), a typical rice field air sample (B), a reagent blank (C), and an air background sample (D).

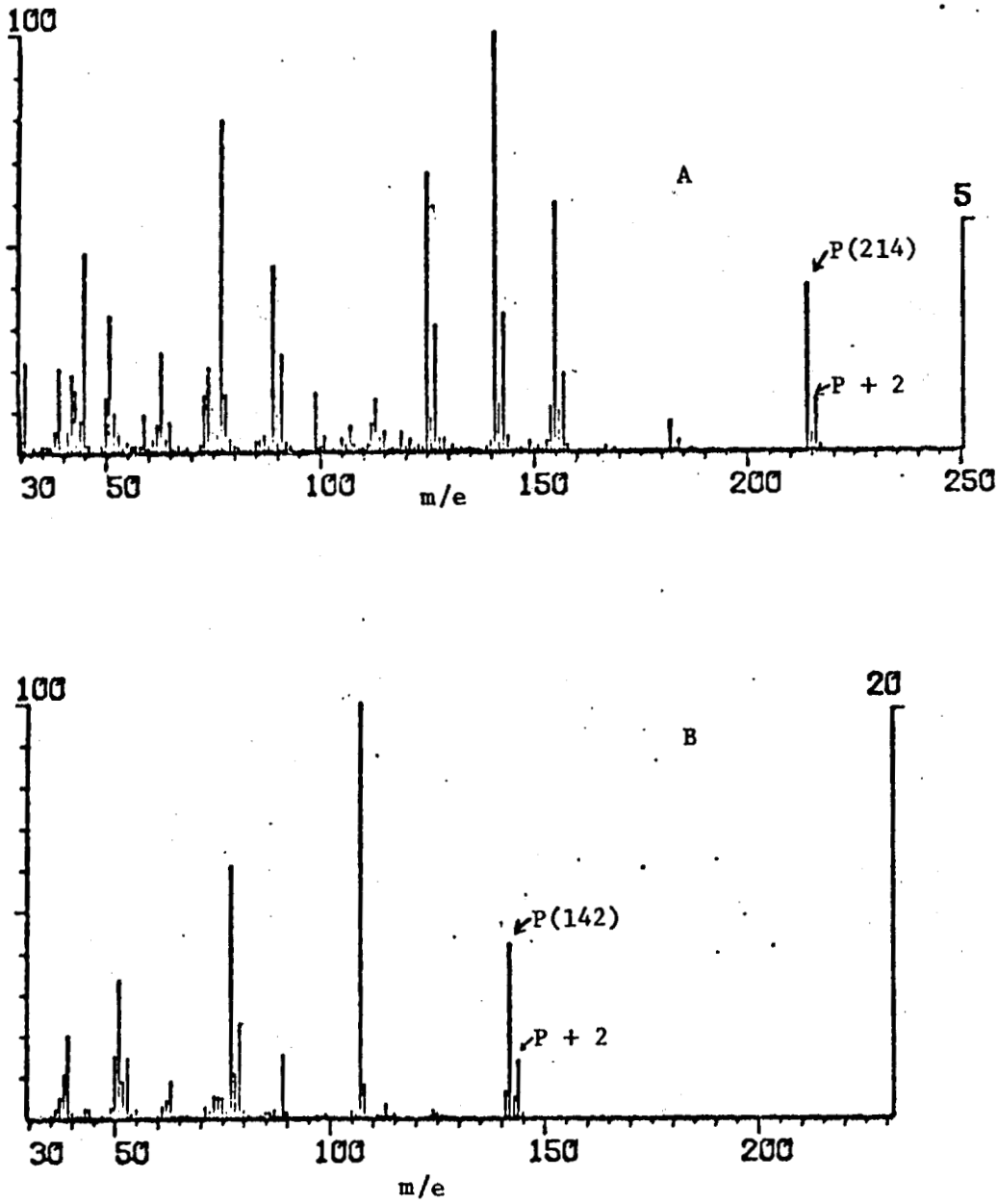

Figure 12. Mass spectra of MCPA (A) and 4-chloro-o-cresol (B) standards.

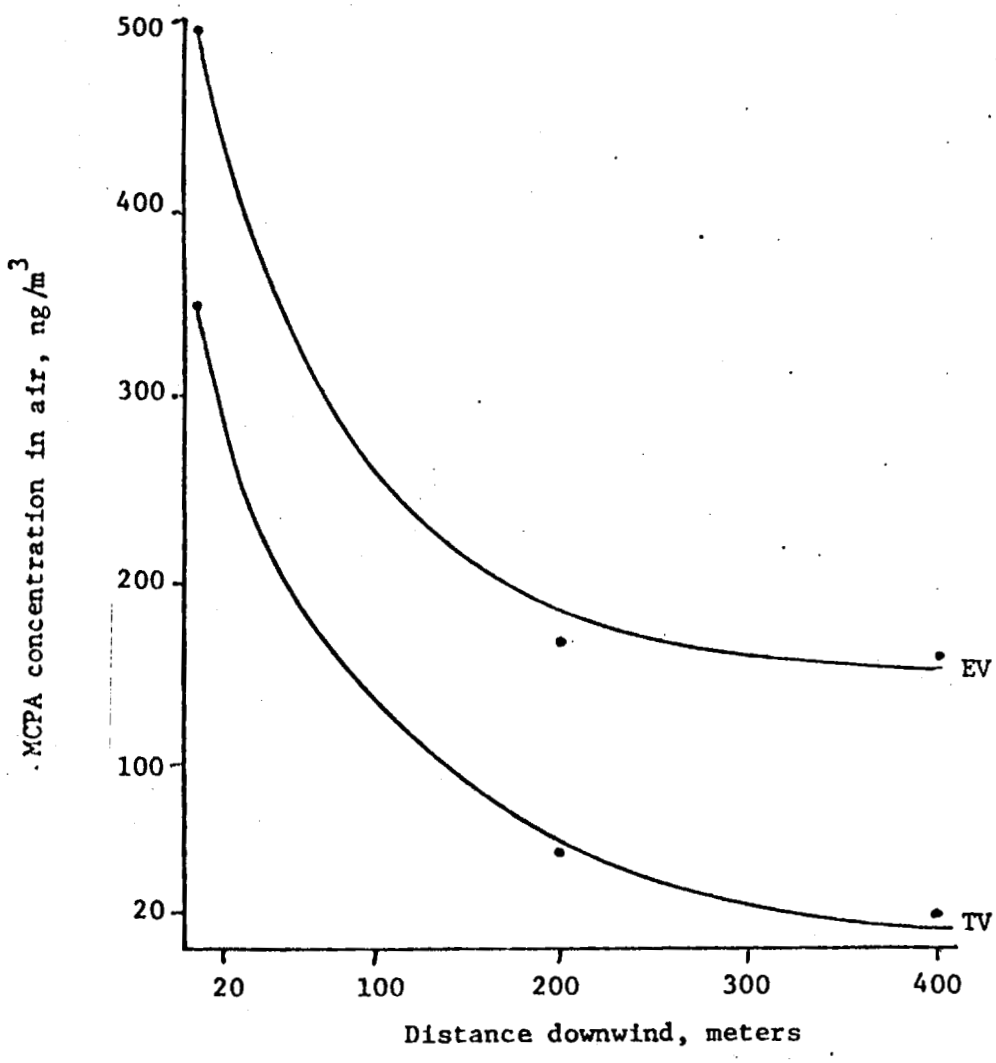

Figure 13. Decline of airborne MCPA with distance during the June 30 application to rice (EV = effective volume; TV = total volume of sampled air).

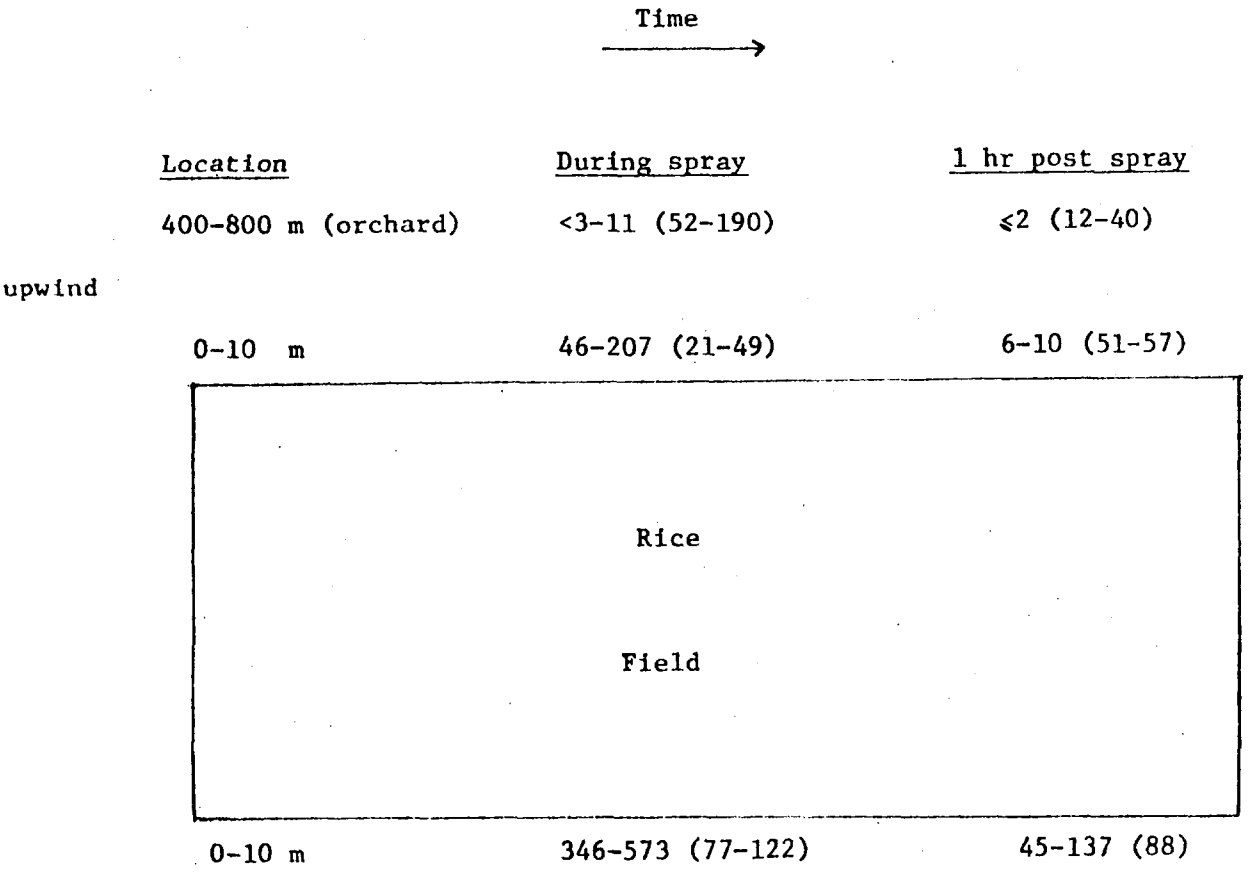

Figure 14. Summary of Tables V and VI. MCPA and (4-CLOC) reported as ng/m^3.

V. FOLIAGE RESIDUES OF MCPA

To complement the atmospheric samples (Part IV), leaf samples were collected from orchards both adjacent to and at a distance from monitored spray applications. The tree species sampled included almond, pistachio, and walnut; samples were collected at time intervals which would span the period from several days pre-spray to 3 months post-spray, although not all locations were sampled at each interval.

Experimental

Sampling. Trees were selected by location in the orchard, marked, and 100 leaves per replicate sample (25 leaves per tree) were taken as uniformly and randomly as possible from throughout the external leaf canopy. In one late-season instance, almond hulls also were collected in a random pattern. Collected leaves from each of 4 trees were composited for each replicate sample and stored separately in glass jars. The jars were then transported cold, in an ice chest, to the laboratory and stored at -30° until analysis. Soil surface samples were collected by means of a portable vacuum collector, and core samples approximately 1 cm in depth and 3600 cm^2 in total area were taken at the same location.

Extraction. Blended dry plant material or soil (25 g) were placed in a Waring blender fitted with a Polytron rotor, with 250 ml of ethyl acetate and 2.5 ml of 1N HCl. The contents were blended for 2 minutes and filtered through anhydrous sodium sulfate (Na_2SO_4) into a glass storage bottle.

Cleanup. The total extract was transferred to a 250 ml round-bottom flask and evaporated to dryness. Ethereal diazomethane solution (5 ml) was added and allowed to react for 10 minutes, 5 ml of benzene was added, and the contents were evaporated to dryness on a rotating evaporator (caution: do not allow sample to evaporate beyond dryness). The residue was dissolved in 5 ml of benzene in preparation for column chromatography.

A cleanup column, 10 cm x 12 mm i.d., containing a 125 ml reservoir was packed with a glass wool pluget, followed in sequence by 1 cm Na_2SO_4, 8 cm of P.R. Grade Florisil, (80-100 mesh, heat treated overnight at 110°C), and finally by 1 cm Na_2SO_4. The column was prewashed with 35 ml of benzene, the sample was transferred to the column with a disposable pipet, the flask was washed with three separate 5 ml washes of benzene, and each washing was transferred to the column just as the previous 5 ml portion disappeared into the top layer of Na_2SO_4. As the last 5 ml of benzene cleared the Na_2SO_4 layer, the collected eluate was removed and discarded. A solution (40 ml) of 5% ethyl ether in benzene was then added to the column, and the eluted methylated MCPA collected into a round-bottom flask.

The collected MCPA fraction was evaporated to 2 ml and again submitted to the Florisil cleanup. The fraction containing the MCPA ester was evaporated to near dryness, transferred to a graduated hematocrit tube, and adjusted to volume with benzene prior to glc analysis with a microcoulometric detector (chloride titration cell). The analytial equipment and conditions were as follows:

Equipment: Dohrmann Model C-200 Microcoulometer; Model G 100 Gas Chromatograph; Model P 100 Furnace Control; Model T-300 Titration Cell.

Pyrolysis oven temperature: 800°C; Block temperature: 200°C.

Column Temperature: 165°C.

Carrier Gas: N_2, 35 ml/min.

Oxidation Gas: O_2, 55 ml/min.

Ohm range setting: 800

Column: 10% DC 200 on Gas Chrom Q, 80-100 mesh, packed in 6' x 1/4" glass column.

Residues were measured by peak height in relation to those of known standards of MCPA methyl ester. MCPA identity was verified in several methylated extracts by gas chromatography-mass spectrometry with a Finnigan Model 3200E instrument and comparison of the resulting mass spectra with those of an authentic standard of MCPA methyl ester.

Results and Discussion

Several analytical methods were examined with an MCPA standard but proved unsatisfactory. Gas chromatography with an electron-capture detector was not sufficiently sensitive and highly subject to interference and attempts to adapt an existing procedure in which MCPA is converted to its highly electron-capturing pentafluorobenzyl ester showed it to be overly sensitive to such variables as time, temperature, and pH during derivatization.

The method of choice was gas chromatography with a microcoulometric (Cl-specific) detector. Analytical recoveries normally were 90-100% at the 0.1 ppm level, and sensitivity normally was 0.01-0.02 ppm. While fortified pistachio leaves resulted in good recovery (90-100%), samples of almond leaves collected in Davis gave a large broad peak near the retention time of MCPA, indicating the presence of a chlorine-containing interference which masked or gave a false-positive value for MCPA. Another sample from unsprayed trees in Davis also contained so many chlorinated interferences that the microcoulometric analytical system became poisoned and required disassembly and cleaning. These difficulties eventually were circumvented by repeated cleanup on Florisil columns, but leaves taken from trees where this study was conducted were free from those interferences.

The results of leaf analysis are shown in Table 14. It is at once striking that all pre-spray samples contained detectable MCPA; its identity was verified by mass spectrometry. In fact, these residue levels were generally similar to those in post-spray samples. As might be expected for residues resulting from

spray drift, MCPA levels on the perimeter row of trees closest to the application site were consistently higher than those on leaves of interior trees, although the interior trees provided remarkably uniform residue values.

During October, 1979, several samples were taken from the Price almond field where MCPA residues had previously been found in samples taken during June, 1979. This study was conducted for purposes of determining possible resistance of MCPA to degradation when adsorbed onto particulate matter on leaf surfaces (leaf strip vs penetrated residues) as compared to penetrated MCPA residues on leaf tissues. We also sampled the soil surface within the orchard (red label) and the dust on the south side of the trees next to the road (blue label). Core samples, approximately 1 cm in depth and 3600 cm^2 total area per sample, were also taken at these locations. Since most chemicals are readily adsorbed into almond hulls and protected from degradation, it was thought desirable to sample some of the few almond hulls that remained on the trees following harvest, and hull samples were taken from the trees within the field (red label) and next to the road (blue label).

No detectable MCPA residues were found in any of the samples (Table 15), clearly showing that MCPA residues do not carry over from one season to the next. The residues found on the preapplication samples taken on 6/7/79 had to come from an application either nearby or from fields far removed. The source of the contamination cannot be determined from this study.

Five samples of almond leaves were also analyzed for chlorocresol. The MCPA chromatographic conditions were used with the one exception, in that the GLC column temperature was 148°C. No residues were found above the detection limit of 0.01 ppm. Samples analyzed were selected from those containing relatively high residues of MCPA and had the following E.T. numbers: 5878C, 5886C,

5886D, 5887C and 5888B. We were not able to analyze the cleaned up extracts for the 4-chloro-2-methyl-N,N-dimethylphenoxyacetamide, as it was lost in the Florisil cleanup for the analysis of MCPA.

Table 14. MCPA residues on orchard leaves from various ranches located in Butte County, CA 1979.

Location	Crop	I.D. Mark	Date Sample	Days From Treatment	E.T. Number	Gross ppm
Price almonds	leaves	Blue Rep I	6-7-79	Pre app	5873B	0.05
"	"	Blue Rep II	"	"	5873C	0.04
"	"	Blue Rep III	"	"	5873D	<0.03
"	"	Blue Rep IV	"	"	5873E	0.04
"	"	Red Rep I	"	"	5873F	<0.03
"	"	Red Rep II	"	"	5873G	0.04
Price almonds	leaves	Blue Rep I	6-17-79	0	5874B	0.12
"	"	Blue Rep II	"	"	5874C	----
"	"	Blue Rep III	"	"	5874D	0.07
"	"	Blue Rep IV	"	"	5874E	0.31
"	"	Red Rep I	"	"	5874F	----
"	"	Red Rep II	"	"	5874G	0.07
Price almonds	leaves	Blue Rep I	6-18-79	1	5875B	0.10
"	"	Blue Rep II	"	"	5875C	0.08
"	"	Blue Rep III	"	"	5875D	0.08
"	"	Blue Rep IV	"	"	5875E	0.07
"	"	Red Rep I	"	"	5875F	0.07
"	"	Red Rep II	"	"	5875G	0.03

Location	Crop	I.D. Mark	Date Sample	Days From Treatment	E.T. Number	Gross ppm
Price almonds	leaves	Blue Rep I	6-23-79	6	5877B	0.10
"	"	Blue Rep II	"	"	5877C	0.15
"	"	Blue Rep III	"	"	5877D	0.18
"	"	Blue Rep IV	"	"	5877E	** 0.42
"	"	Red Rep I	"	"	5877F	-----
"	"	Red Rep II	"	"	5877G	0.07
Price almonds	leaves	Blue Rep I	6-29-79	12	5878B	0.23
"	"	Blue Rep II	"	"	5878C	0.26
"	"	Blue Rep III	"	"	5878D	**0.20
"	"	Blue Rep IV	"	"	5878E	0.08
"	"	Red Rep I	"	"	5878F	0.06
"	"	Red Rep II	"	"	5878G	0.05
Price almonds	leaf strip	Blue Rep I	10-3-79	108	5892BI	<0.01
"	Penetrate	"	"	"	5892BII	<0.01
"	leaf strip	Blue Rep II	"	"	5892CI	<0.01
"	Penetrate	"	"	"	5892CII	<0.01
"	leaf strip	Blue Rep III	"	"	5892DI	<0.01
"	Penetrate	"	"	"	5892DII	<0.01
"	leaf strip	Blue Rep IV	"	"	5892EI	<0.01
"	Penetrate	"	"	"	5892EII	<0.01
"	leaf strip	Red Rep I	"	"	5892FI	<0.01
"	Penetrate	"	"	"	5892FII	<0.01
"	leaf strip	Red Rep II	"	"	5892GI	<0.01
"	Penetrate	"	"	"	5892GII	<0.01

** Residues confirmed by GC/MS

Location	Crop	I.D. Mark	Date Sample	Days From Treatment	E.T. Number	Gross ppm
McClintock almonds	leaves	Red	6-7-79	Pre app	5885B	<0.01
McClintock almonds	leaves	Blue Rep I	6-22-79	0	5886B	0.26
"	"	Blue Rep II	"	"	5886C	**0.45
"	"	Blue Rep III	"	"	5886D	0.46
"	"	White Rep I	"	"	5886E	0.08
"	"	White Rep II	"	"	5886F	0.06
"	"	Blue Rep I	6-23-79	1	5887B	0.27
"	"	Blue Rep II	"	"	5887C	**0.41
"	"	Blue Rep III	"	"	5887D	0.29
"	"	White Rep I	"	"	5887E	0.03
"	"	White Rep II	"	"	5887F	0.07
McClintock almonds	leaves	Blue Rep I	6-29-79	7	5888B	0.38
"	"	Blue Rep II	"	"	5888C	**0.35
"	"	Blue Rep III	"	"	5888D	0.28
"	"	White Rep I	"	"	5888E	0.04
"	"	White Rep II	"	"	5888F	0.08
McClintock almonds	leaf strip	Blue Rep I	10-3-79	103	5893BI	<0.01
	Penetrate	"	"	"	5983BII	<0.01
"	leaf strip	Blue Rep II	"	"	5893CI	<0.01
"	Penetrate	"	"	"	5893CII	<0.01
"	leaf strip	Blue Rep III	"	"	5893DI	<0.01
"	Penetrate	"	"	"	5893DII	<0.01
"	leaf strip	White Rep I	"	"	5893EI	<0.01
"	Penetrate	"	"	"	5893EII	<0.01
"	leaf strip	White Rep II	"	"	5893FI	<0.01
"	Penetrate	"	"	"	5893FII	<0.01

Location	Crop	I.D. Mark	Date Sample	Days From Treatment	E.T. Number	Gross ppm
Peterson Pistachioes	leaves	Blue West	6-7-79	Pre app	5879B	<0.01
"	"	White South	"	"	5879C	<0.01
"	"	Red Inside	"	"	5879D	<0.01
Peterson Pistachioes	leaves	Blue West	6-17-79	0	5880B	0.02
"	"	White South	"	"	5880C	0.03
"	"	Red Inside	"	"	5880D	<0.01
Peterson Pistachioes	leaves	Blue West	6-18-79	1	5881B	0.02
"	"	White South 1st Tree Only	"	"	5881C	0.01
"	"	Red Inside	"	"	5881D	----
Peterson Pistachioes	leaves	Blue West	6-22-79	5	5882B	<0.01
"	"	White South	"	"	5882C	<0.01
"	"	Red Inside	"	"	5882D	<0.01
Peterson Pistachioes	leaves	Blue West	6-23-79	6	5883B	<0.01
"	"	White South	"	"	5883C	<0.01
"	"	Red Inside	"	"	5883D	<0.01
Peterson Pistachioes	leaves	Blue West	6-29-79	12	5884B	0.02
"	"	White South	"	"	5884C	0.02
"	"	Red Inside	"	"	5884D	0.02
McClintock Walnuts	leaves	Red Rep I	6-22-79	0	5889B	0.32
"	"	Red Rep II	"	"	5889C	0.35
"	"	Red Rep I	6-23-79	1	5890B	0.33
"	"	Red Rep II	"	"	5890C	0.23

Location	Crop	MCPA ID Mark	Date Sampled	Days from Treatment	ET Number	* Gross PPM
McClintock Walnuts	leaves	Red Rep I	6-29-79	7	5891B	0.21
McClintock Walnuts	"	Red Rep I	"	"	5891C	0.27
McClintock almonds 10th tree from S.E. corner front row	leaves	B-6	6/19/79	-3	5894B	0.06
McClintock almonds 5th tree from S.E. corner	leaves	B-10	6/19/79	-3	5894C	0.07
McClintock almonds 5th tree west + 5 trees north of S.E. corner	leaves	B-5	6/20/79	-2	5894D	0.03
McClintock almonds 4th tree in from south	leaves	B-9	6/20/79	-2	5894E	0.06
McClintock almonds 5 trees in diaganol	leaves	W-15	7/01/79	+9	5894F	0.03
McClintock almonds 5 trees in diaganol	leaves	W-14	7/01/79	+9	5894G	0.03
McClintock almonds 1st row	leaves	W-13	7/01/79	+9	5894H	0.07
McClintock almonds 1st row	leaves	W-3	7/01/79	+9	5894I	0.16
Martinez almonds trees front row	leaves	B-4	6/19/79	-3	5895B	0.21
Martinez almonds east trees near corner of rice field	leaves	B-7	6/19/79	-3	5895C	0.14
Martinez almonds 5 trees in	leaves	B-11	6/20/79	-2	5895D	0.08
Martinez almonds day + 1 1st row	leaves	W-17	6/23/79	+1	5895E	0.09
Martinez almonds 5 trees in from end day + 1	leaves	W-18	6/23/79	+1	5895F	0.04

Location	Crop	MCPA ID Mark	Date Sampled	Days from Treatment	ET Number	Gross PPM
Martinez almonds 1st row day + 1	leaves	W-21	6/23/79	+1	5895G	0.24
Martinez almonds 5 trees in from row day + 1	leaves	W-23	6/23/79	+1	5895H	0.05
Martinez almonds 1st row	leaves	W-9	7/01/79	+9, +1	5895I	0.10
Martinze almonds 5 trees in	leaves	W-10	7/01/79	+9, +1	5895J	0.07
Martinez almonds 1st row	leaves	W-12	7/01/79	+9, +1	5895K	0.15
Martinez almonds 5 trees in	leaves	W-11	7/01/79	+9, +1	5895L	0.07
Martinez almonds 5 rows in	leaves	W-26	7/17/79	+26, +18	5895M	0.07
Martinez almonds front row	leaves	W-24	7/17/79	+26, +18	5895N	0.08
Martinez almonds front row	leaves	W-24	7/17/79	+26, +18	5895O	0.09
Montgomery almonds	leaves	B-8	6/19/79	-3	5896B	0.19
Montgomery almonds east tree	leaves	B-2	6/19/79	-3	5896C	0.09
Montgomery almonds 5 trees in from edge	leaves	B-6	6/20/79	-2	5896D	0.06
Montgomery almonds 5 trees in	leaves	B-1	6/20/79	-2	5896E	0.04
Montgomery almonds 5 trees in day + 1	leaves	W-19	6/23/79	+1	5896F	0.04
Montgomery almonds 1st row day + 1	leaves	W-20	6/23/79	+1	5896G	0.08
Montgomery almonds 1st row tree day + 1	leaves	W-27	6/23/79	+1	5896H	0.08
Montgomery almonds 5-trees in from south	leaves	W-1	7/01/79	+9	5896I	0.08

Location	Crop	MCPA ID Mark	Date Sampled	Days from Treatment	ET Number	Gross PPM
Montgomery almonds 1st row	leaves	W-6	7/01/79	+9	5896J	0.12
Montgomery almonds 1st row	leaves	W-7	7/01/79	+9	5896K	0.16
Montgomery almonds 5-trees in from south	leaves	W-8	7/01/79	+9	5896L	0.06
Petersons Pistachios outer S.W. corner	leaves	W-2	7/01/79	+9	5897B	0.02
Petersons Pistachios outer S.W. Corner	leaves	W-4	7/01/79	+9	5897C	0.02
Petersons Pistachios outer S.W. corner	leaves	W-16	7/01/79	+9	5897D	0.02
Petersons Pistachios 4 trees in from So.	leaves	W-5	7/01/79	+9	5897E	0.02

Table 15. MCPA residues on dust and almond hulls.

Location	Crop	MCPA ID Mark	Date Sampled	Days from Treatment	ET Number	Gross PPM
Price almond orchard	Dust + filters	Blue rep I & II	10/03/79	108	5899B	<0.01
Price almond orchard	Dust + filters	Blue rep III & IV	10/03/79	108	5899C	<0.01
Price almond orchard	Dust + filters	red rep I & II	10/03/79	108	5899D	<0.01
Price almond orchard	Dust + filter	Road Dust	10/03/79	108	5899E	<0.01
Price almond orchard	Soil core	Blue rep I & II	10/03/79	108	5899F	<0.01
	Soil core	Blue rep III & IV	10/03/79	108	5899G	<0.01
Price almond orchard	Soil	Red Rep I & II	10/03/79	108	5899H	<0.01
Price almond orchard	Almond hulls	Red inside	10/03/79	108	5B98C	<0.01
Price almond orchard	Almond hulls	Blue outside	10/03/79	108	5898B	<0.01

VI. GENERAL CONCLUSIONS

MCPA (4-chloro-2-methylphenoxyacetic acid), usually applied as the dimethylamine salt, has become the principal herbicide for control of broadleaf weeds in Central Valley rice. The 1979 application to a monitored area in central Butte County, California, involved only a single aerial spraying to each of several flooded rice fields at a rate of approximately one pound per acre as an aqueous solution under conditions specified and monitored by the County Agricultural Commissioner.

The purity of spray concentrate--as determined by gas chromatography, high-pressure liquid chromatography, and mass spectrometry--was very high. The principal impurity was 2-methylphenoxyacetic acid (1%), with smaller amounts of other chlorinated phenoxyacetic acids; the only neutral impurity occuring above about 1 ppm was MCPA dimethylamide, and no dioxins or dibenzofurans were detectable at this level.

However, despite climatic safeguards, application efficiency and uniformity appeared to be much lower than expected, and a significant proportion of the spray may have been dispersed into the atmosphere. The use of high-volume air samplers, equipped with macroreticular resin adsorbent, was generally satisfactory for the collection of air samples (efficiency >80%), and microcoulometric gas chromatography (Cl-specific) of methylated residues permitted quantitative analysis down to 3 ng/m^3 for one-hour collection periods and less than 1 ng/m^3 for long-term collections. The microcoulometric method also was best for the analysis of foliage samples; other analytical procedures resulted in low recoveries, very high blank values, and/or the introduction of chemical interferences which would lead to false-positive readings. The identity of both airborne and foliage residues was positively confirmed by mass spectrometry.

MCPA/DMA spray formulations proved to be very rapidly degraded by sunlight. The principal breakdown product, chlorocresol (4-chloro-2-methylphenol), was accompanied by other volatile phenols and MCPA dimethylamide. In thin films or droplets, the MCPA was over 50% degraded within the first day, and degradation was largely complete within a week to produce a mixture primarily containing unidentified acids. The chlorocresol volatilized into the surrounding atmosphere as it formed.

Analysis revealed the presence of both MCPA and chlorocresol in the atmosphere immediately following spray applications. Although the levels were lower at the upwind edge of the sprayed rice fields than at the downwind edge, the upwind incursion was very definite. As might be expected, atmospheric residues declined with downwind distance from the source and with time, although the increasing ratio of chlorocresol to MCPA reflected both photochemical degradation in the spray and eventual degradation and volatilization from water and leaf surfaces. Although the residue levels from any specific application eventually will reach low values, measurable residues may be found for several kilometers downwind.

However, Sacramento Valley applications of MCPA are concentrated into a relatively restricted area representing those portions of eight counties which border on river systems. The period of application is short--normally about three weeks in late June and early July, and during that period in 1979, roughly 457,000 pounds of actual MCPA/DMA were applied to the area. It is not surprising that within several days of the start of the spray period, there developed a significant ambient background level of atmospheric MCPA which influenced all subsequent monitoring results.

This residue background becomes of particular significance in orchards adjacent to the rice fields. Air sampling within the orchards during and after the spraying revealed low but rather consistent MCPA and chlorocresol levels although the trees were upwind and protected by a buffer zone. MCPA residues indeed were detectable on foliage, although the highest value was 0.24 ppm and more typical positive values were 0.05-0.10 ppm; however, the analytical data not only indicate the probable reinforcement of the initial residues by later spray applications to more distant fields but also the presence of comparable residues of MCPA even before general spraying in the monitoring area. Perhaps due to volatilization, chlorocresol residues were not detected on foliage, and any MCPA amide was sacrificed in the analytical process.

Foliage and fruit samples collected 3 months after the nearby spraying contained no detectable residues when analyzed by a method which would measure the principal known MCPA metabolites as well as absorbed and surface MCPA. Dust from the orchard floor and adjacent roadway likewise contained no measurable MCPA at that time. Therefore, the pre-spray leaf residues probably do not represent carryover from a previous season's spraying but rather drift from early MCPA spray applications observed at distances of several kilometers. About 2% of the total MCPA/DMA used in the 8 counties was applied to wheat, oats, and barley during Winter and Spring months and conceivably could make a small contribution to the residues detected later.

However, it is these winter and spring applications, or the similar and more extensive use of 2,4-D, which might be expected to cause formative effects in emerging new foliage. Neither new nor mature leaves showed obvious signs of damage from normal rice field applications--microscopic examination was beyond

the scope of this project--although accidentally-sprayed foliage was severely damaged and showed that absorption can occur. The absence of hydrolyzable fixed metabolites seems peculiar, but could indicate a reduced ability of mature leaves of tree species to absorb the DMA salt at low exposures. A much more extensive investigation would be required to reveal long-term damage to the trees or to harvest yields, but such effects are not ruled out by the present evidence.

The movement of the spray drift is not too surprising. The prevailing summer wind in the test area is from the south; that is, the orchards generally are downwind from treated fields. Although the rule restricting spray applications to the brief periods of northerly wind doubtless protects the trees from the most direct spray, even the buffer zone can only reduce atmospheric dispersion of spray and vapor caused by turbulence and rapidly-changing wind patterns. This constant mixing produces a fairly uniform concentration of 5-10 ng/m^3 in air during the spray season which then drops below the detection level by mid-August; continued photolysis and volatilization would tend to maintain chlorocresol levels well past the application period.

The effects of chlorocresol remain unknown, as does its atmospheric fate. In water or spray, it is degraded by oxidation and hydrolysis about as rapidly as is MCPA/DMA; degradative reactions in the vapor state probably would be different, if indeed they occur. That chlorocresol eventually becomes the principal atmospheric residue suggests that its own degradation may be slow.

Although this investigation was not directly concerned with human health implications of MCPA spraying, several observations may be pertinent. MCPA has received substantial toxicological attention during the past few years.

Gurd et al (1965) showed that MCPA salts were only moderately toxic to rats (acute oral LD_{50} 800 mg/kg as diethanolamine salt) and mice (acute oral LD_{50} 550 mg/kg as diethanolamine salt and 560 mg/kg as Na salt). Ninety day feeding of rats at 50 ppm in the diet showed no effect on growth, food intake, mortality, biochemistry, organ weight, or histopathology, and the erythema produced by continuous contact of rabbit skin with 500 mg/kg MCPA for 3 weeks was reversible when the agent was removed; more severe effects were observed at higher doses (Verschuuren et al, 1975). The acute ip LD_{50} of chlorocresol in rats was shown to be 1190 mg/kg, but 100 mg/kg/day ip for 4 weeks affected only the intestinal mucosa (Hattula et al, 1979).

Ingestion of MCPA ethyl ester by pregnant rats resulted in no adverse fetal effects at either 40 or 500 ppm in the diet during days 8 to 15 of gestation (Yasuda and Maeda, 1972); human males cleared a 5 mg dose of MCPA within 5 days, during which all clinical tests showed normalcy (Fjelstad and Wannag, 1977), although mild changes occurred in seminiferous epithalamium of some rats following ingestion of water containing 100 mg/L of MCPA sodium salt (Elo and Parvinen). MCPA and its metabolites were not mutagenic in bacteria (Ames assay) (Räsänen et al, 1977).

Aside from accidental massive exposure, measureable effects from oral or dermal exposure to MCPA salts during or after normal spraying operations seem unlikely, and exposure to chlorocresol through these routes would be negligible. However, no information on inhalation toxicology of either substance has appeared in the literature, and their solubility in both water and organic solvents suggests that penetration into the lung might be possible; although the atmospheric levels of the two compounds suggest that the dose probably would never exceed 0.5 µg/hr, future consideration of inhalation effects may be advisable.

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Gurd, M.R., G.L.M. Harmer, and B. Lessel. Food Cosmet. Toxicol. 3, 883 (1965).

Hattula, M.L., H. Reunanen, and A.U. Arstila. Bull. Environ. Contam. Toxicol. 21, 492 (1979).

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Appendix IA

USE OF MCPA AMINE SALT IN EIGHT CALIFORNIA COUNTIES

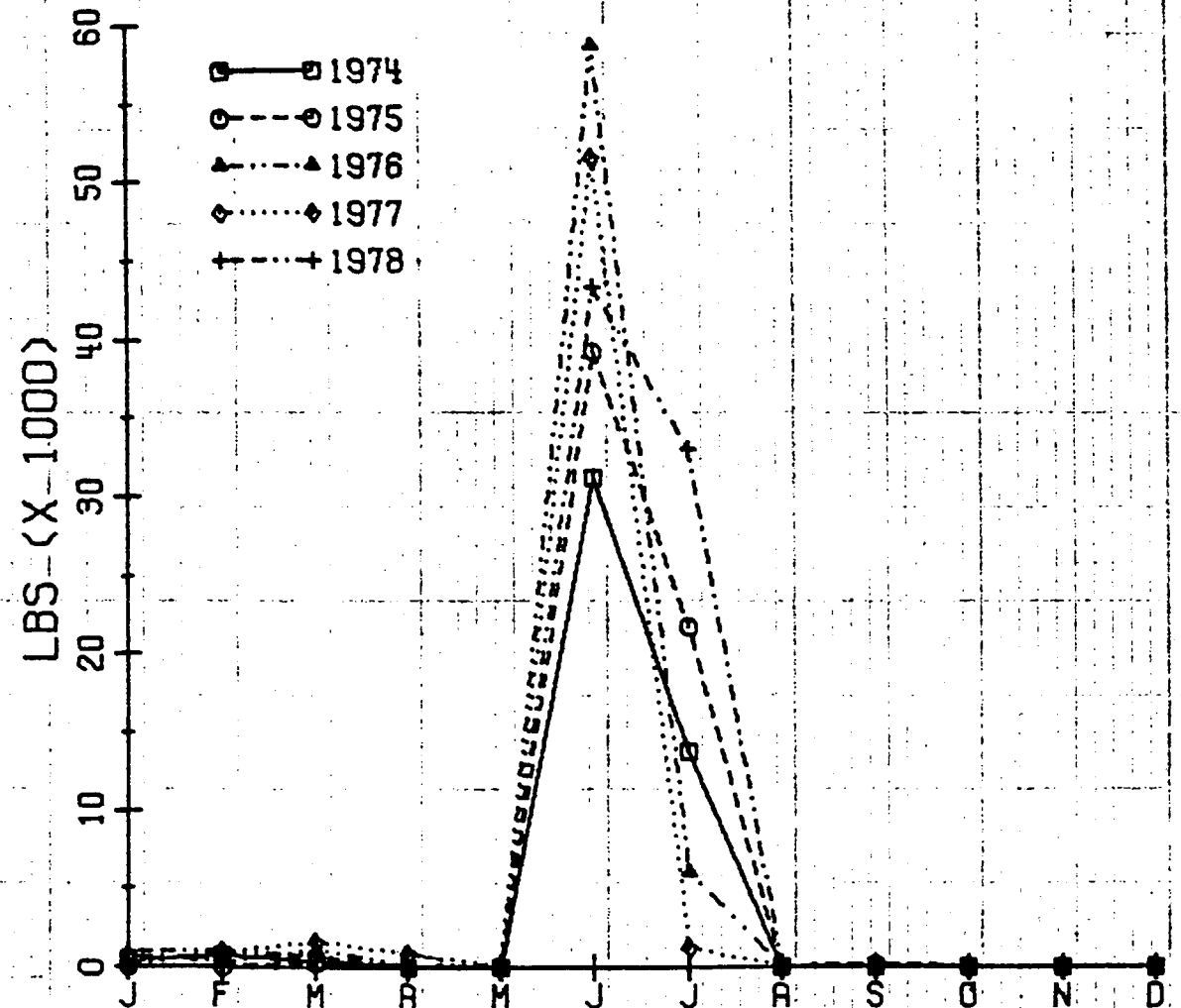
BY MONTH AND YEAR, 1974 - 78

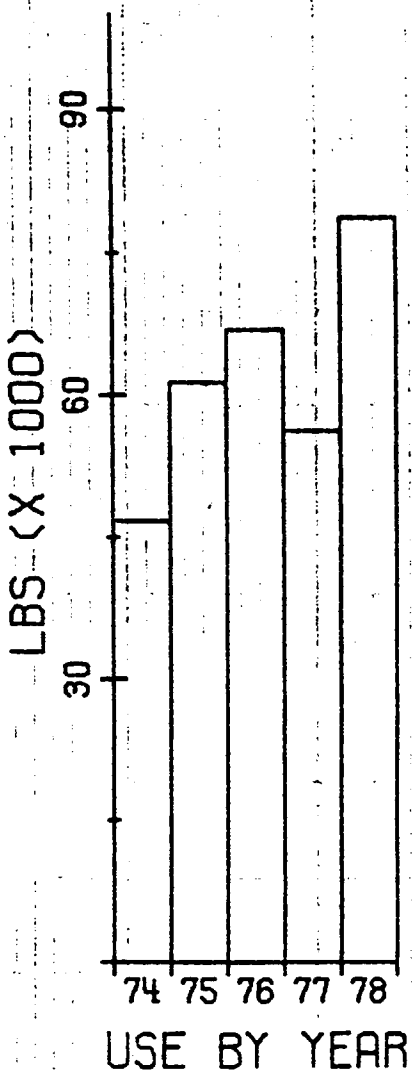
Appendix IB

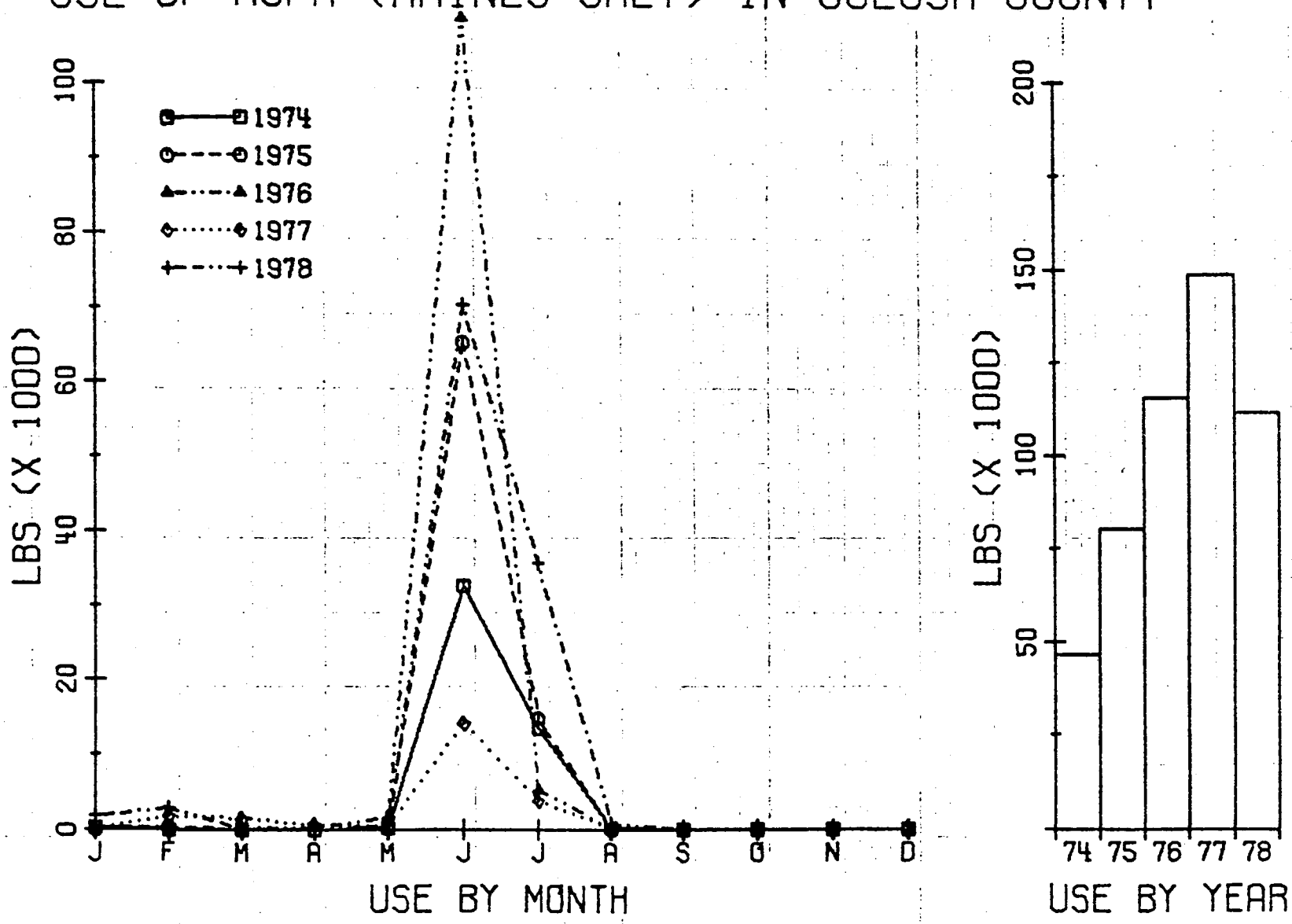
USE OF ALL OTHER MCPA DERIVATIVES IN EIGHT CALIFORNIA

COUNTIES BY MONTH AND YEAR, 1974 - 78

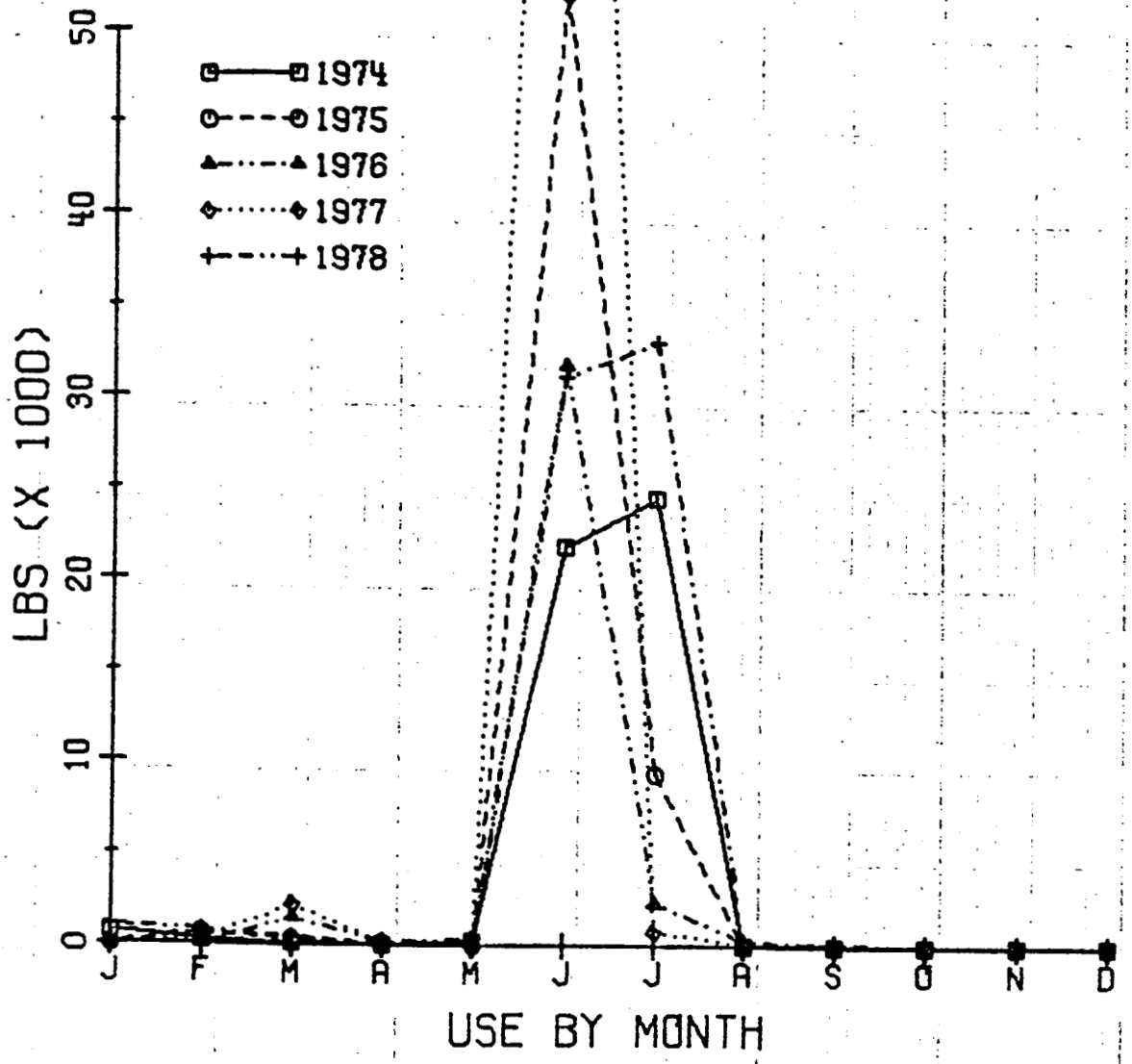
USE OF MCPA (AMINES SALT) IN BUTTE COUNTY

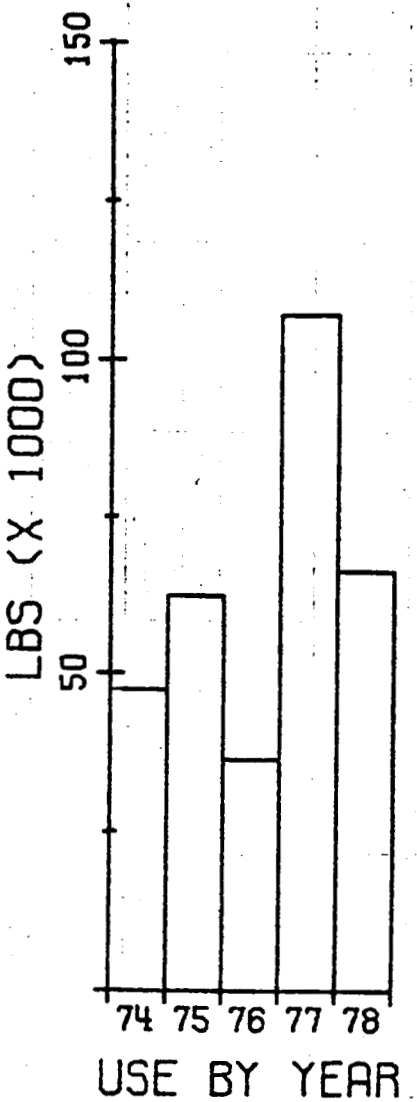




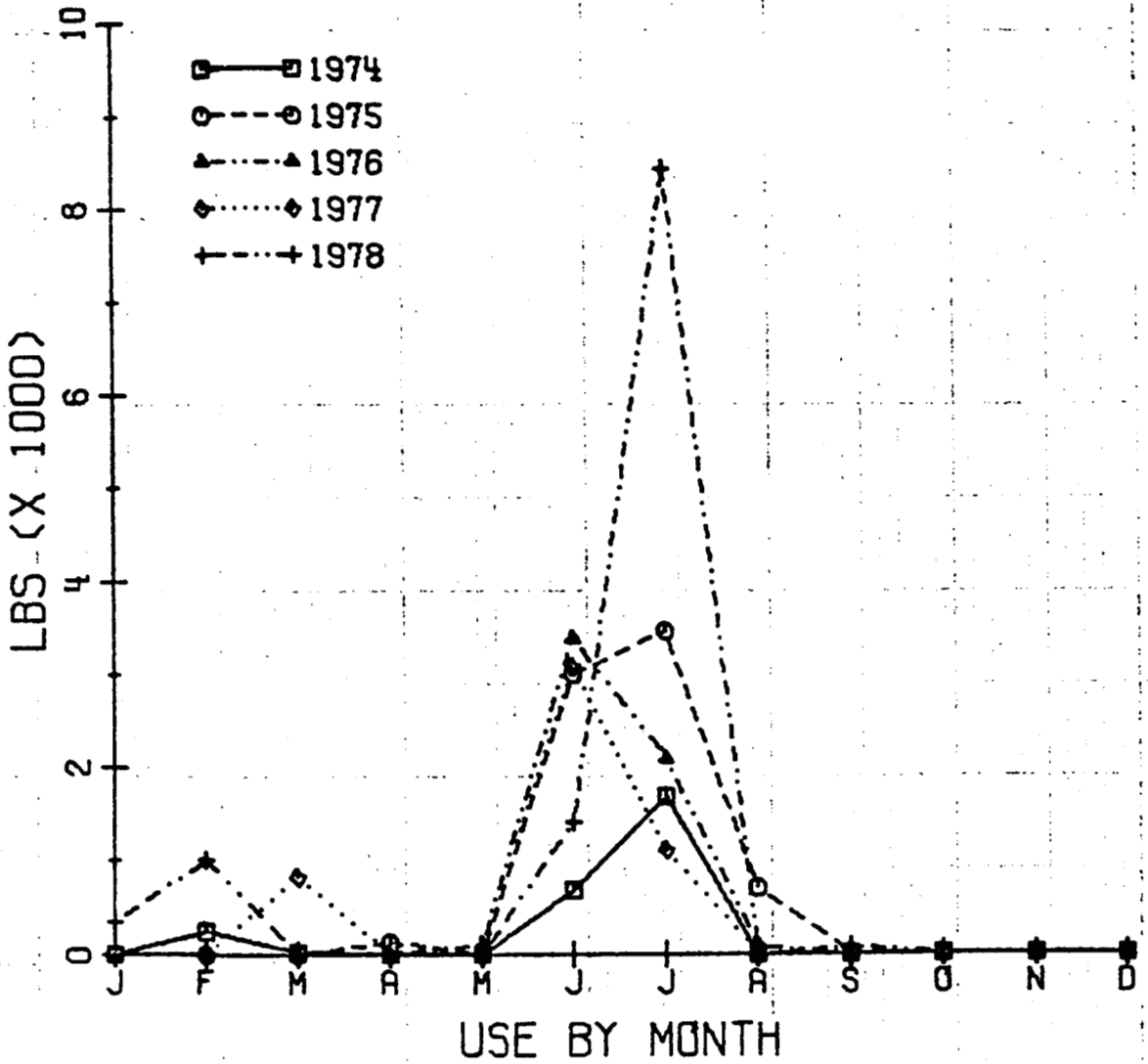

USE OF MCPA (AMINES SALT) IN COLUSA COUNTY
LBS (X 1000)
100
80
60
40
20
0
1974
1975
1976
1977
1978
J F M A M J J A S O N D
USE BY MONTH
LBS (X 1000)
200
150
100
50
74 75 76 77 78
USE BY YEAR

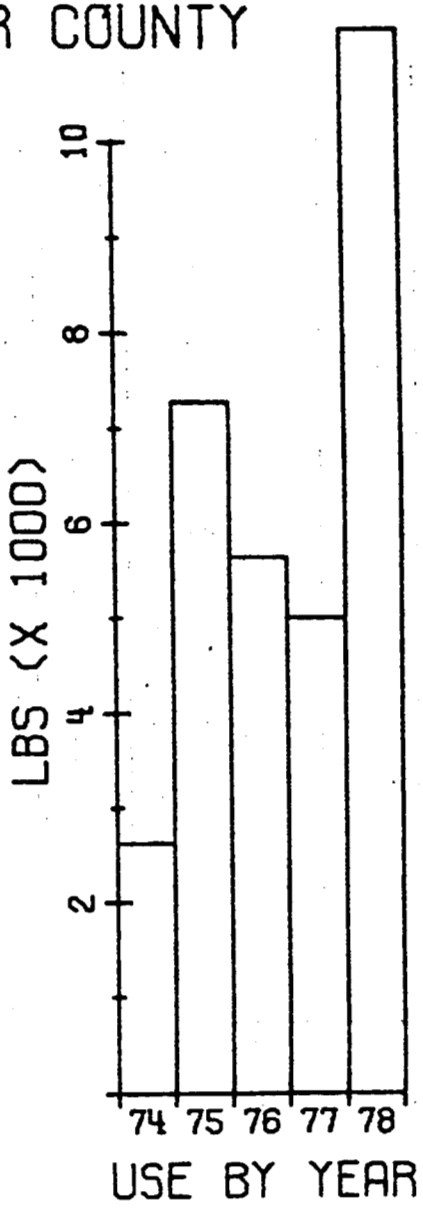
USE OF MCPA (AMINES SALT) IN GLENN COUNTY



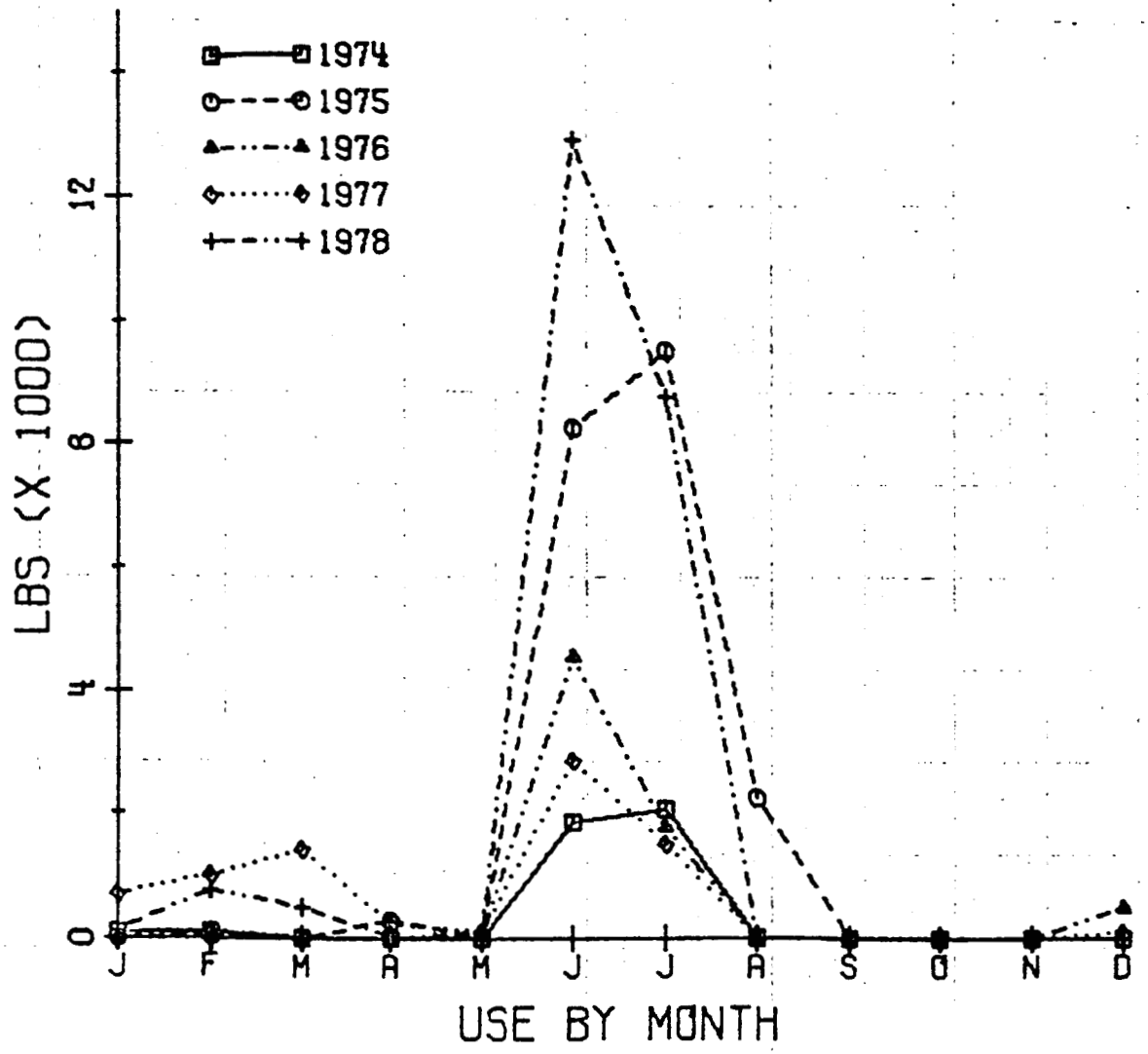


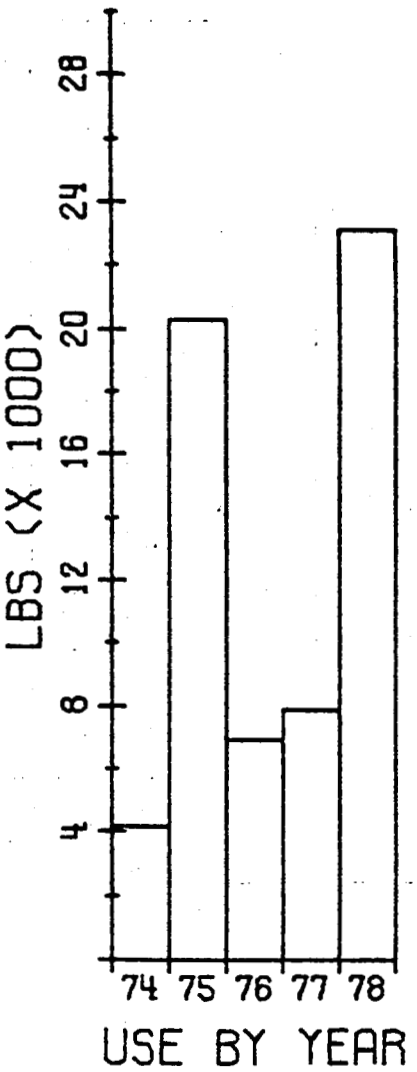
USE OF MCPA (AMINES SALT) IN PLACER COUNTY



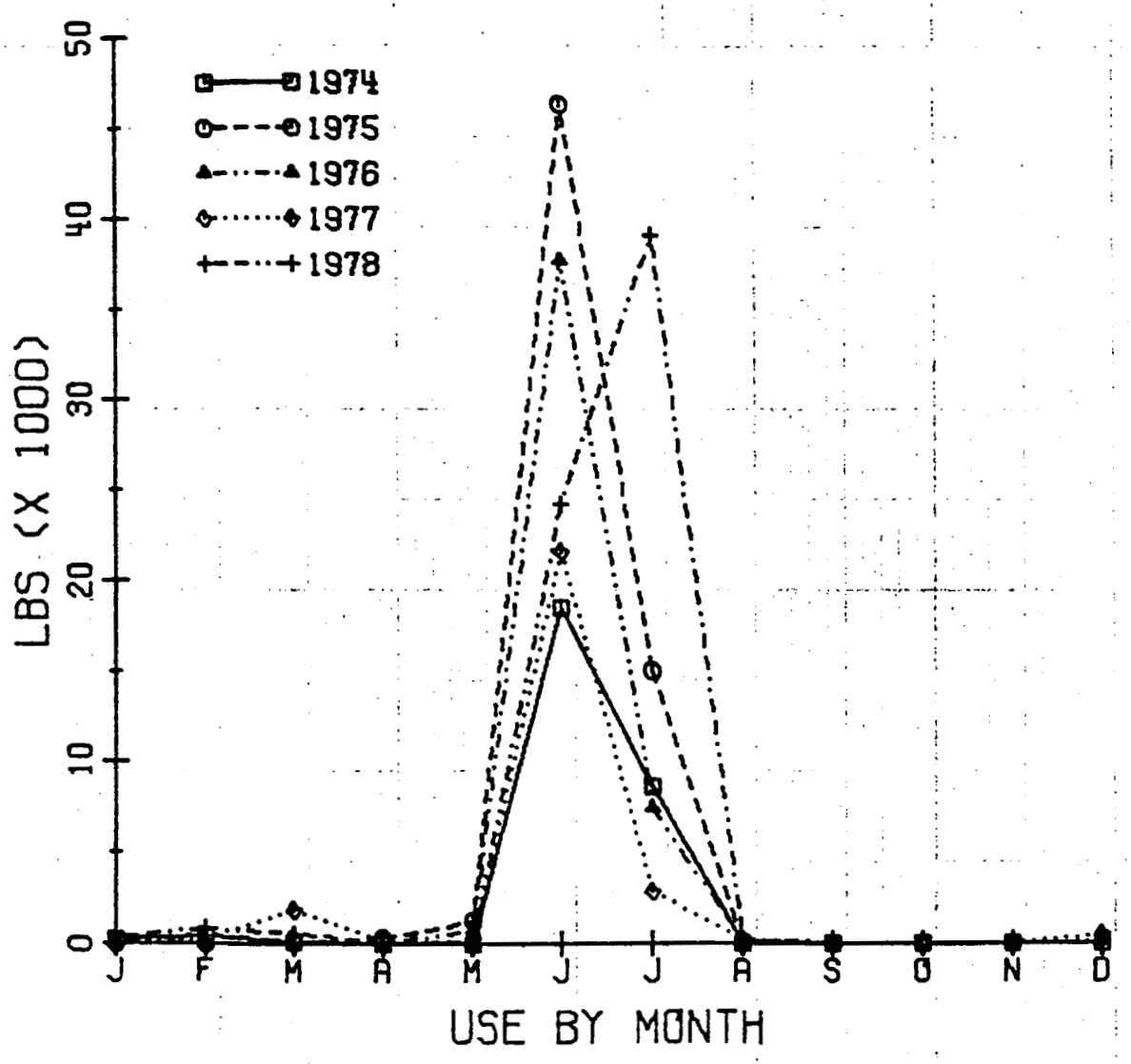


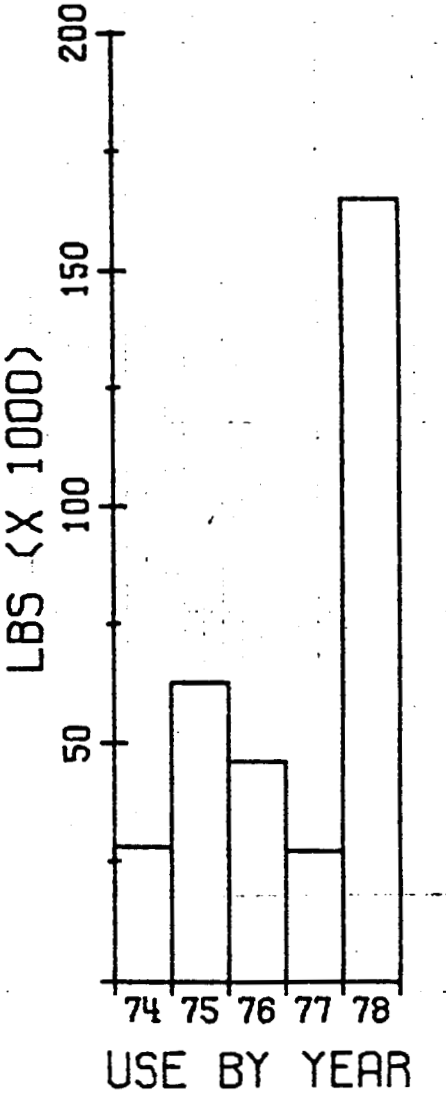
USE OF MCPA (AMINES SALT) IN SACRAMENTO COUNTY



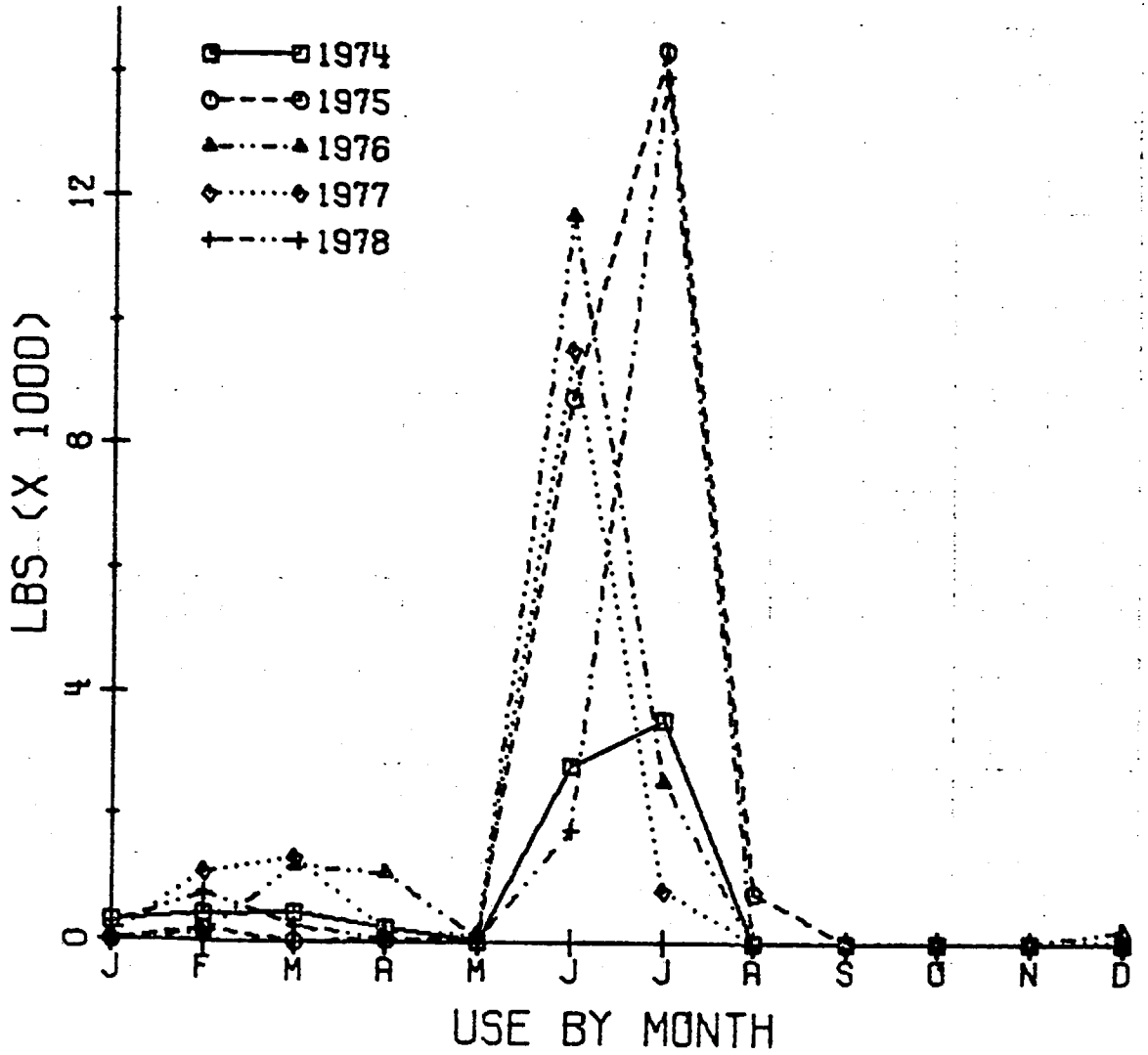


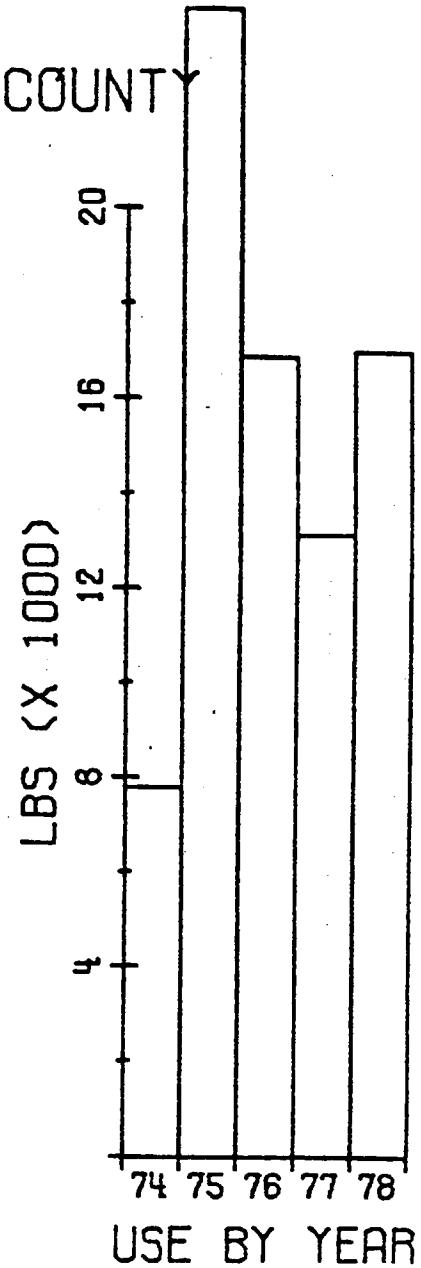
USE OF MCPA (AMINES SALT) IN SUTTER COUNTY



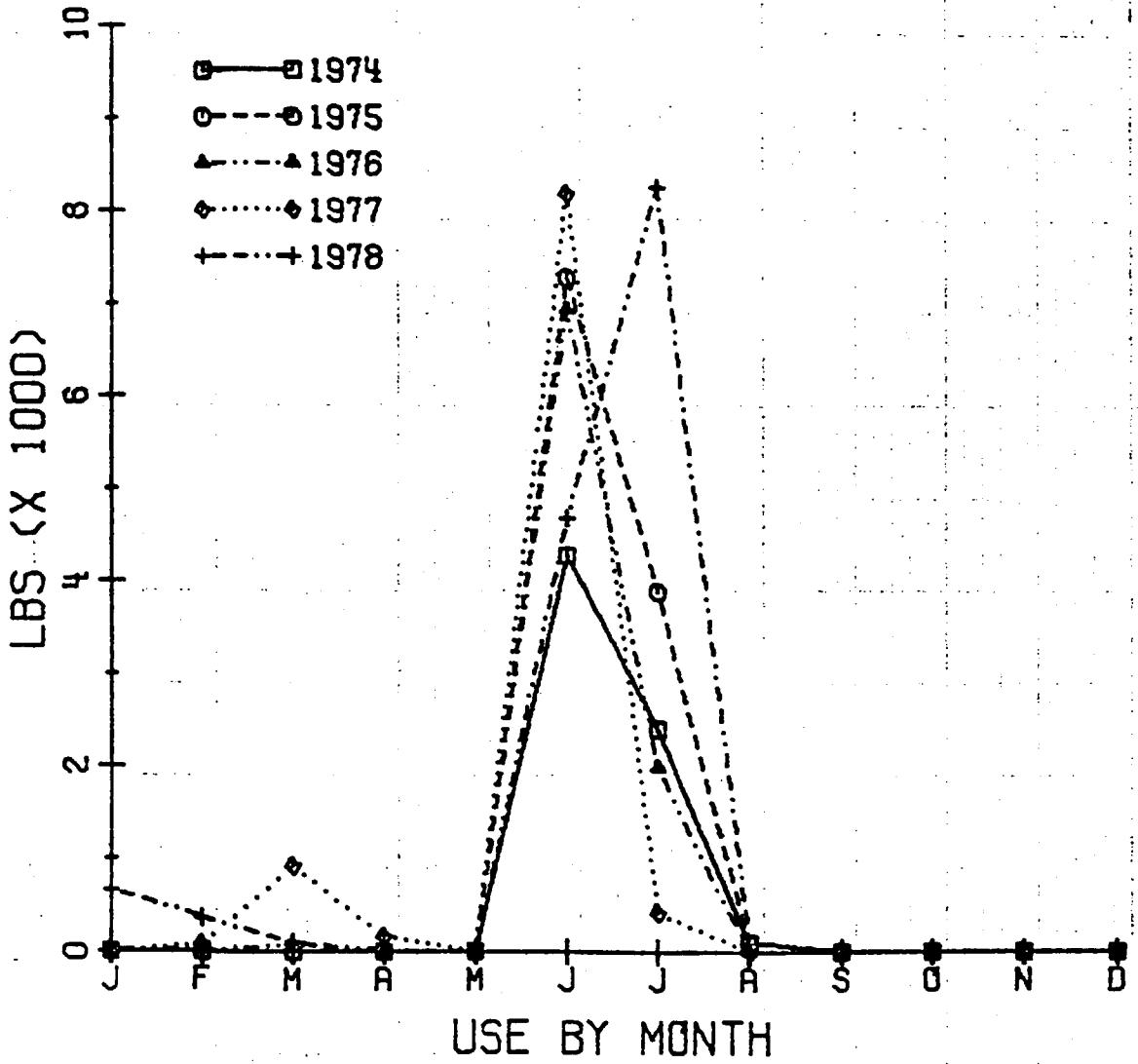


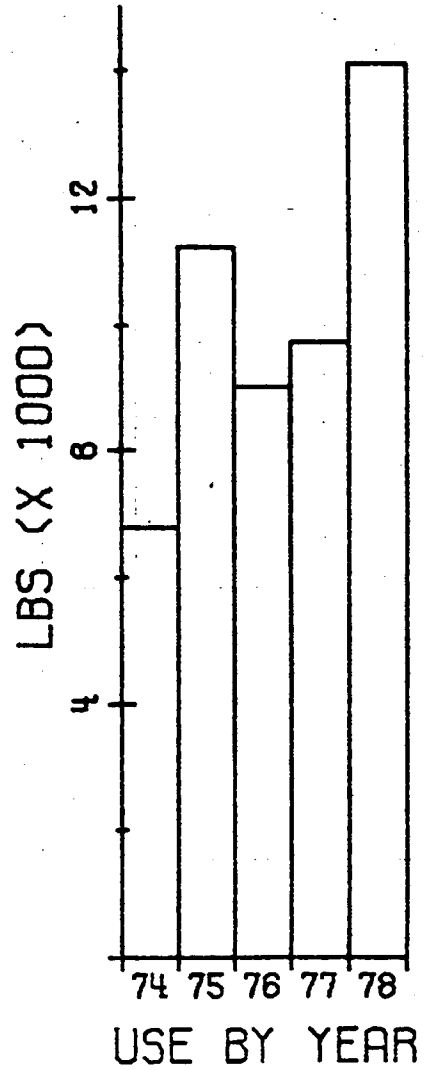
USE OF MCPA (AMINES SALT) IN YOLO COUNTY



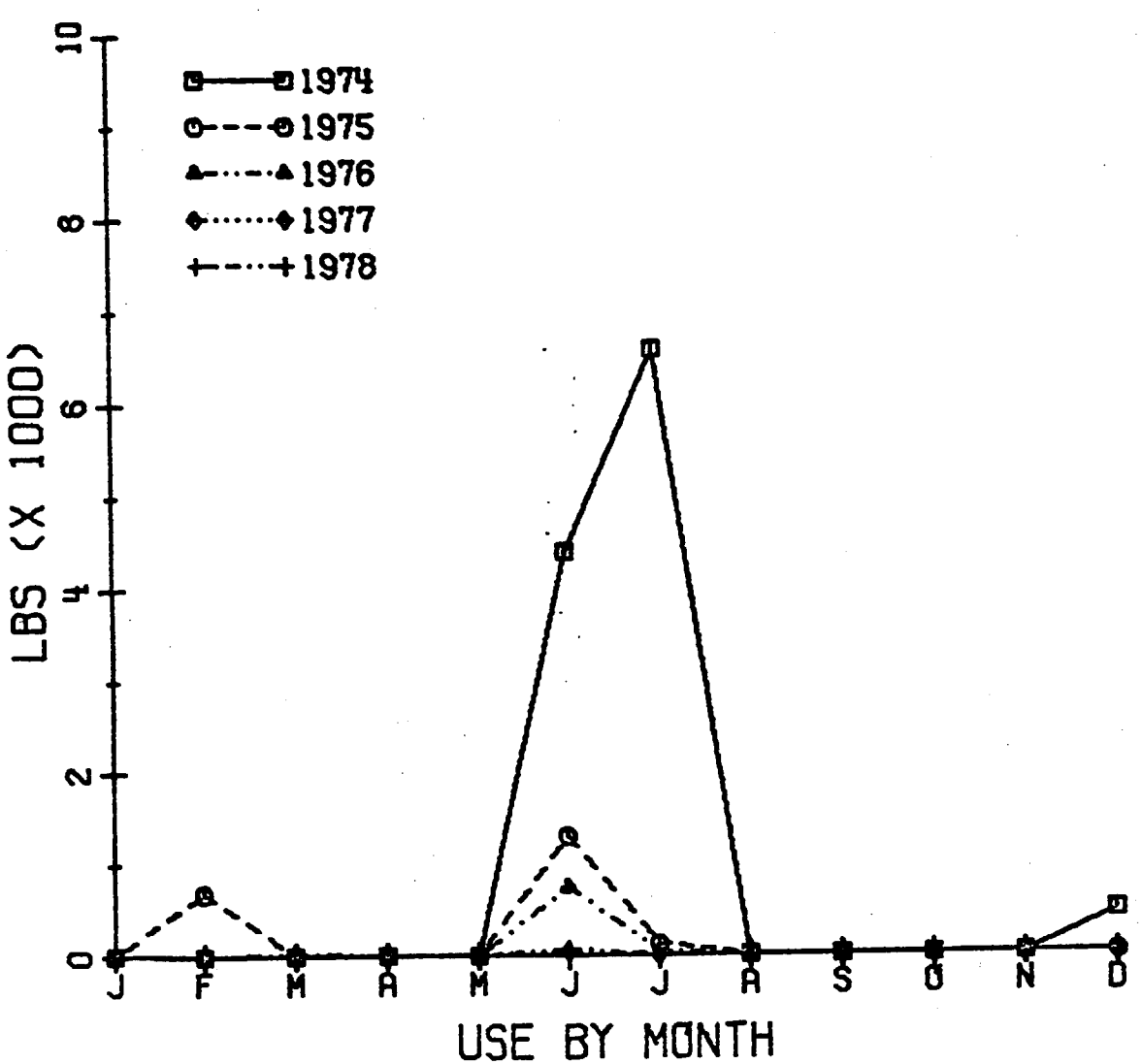


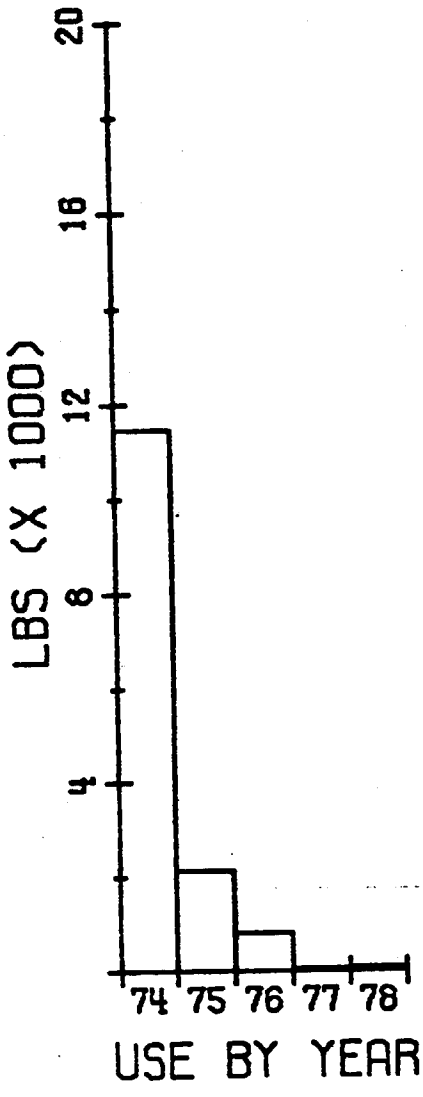
USE OF MCPA (AMINES SALT) IN YUBA COUNTY



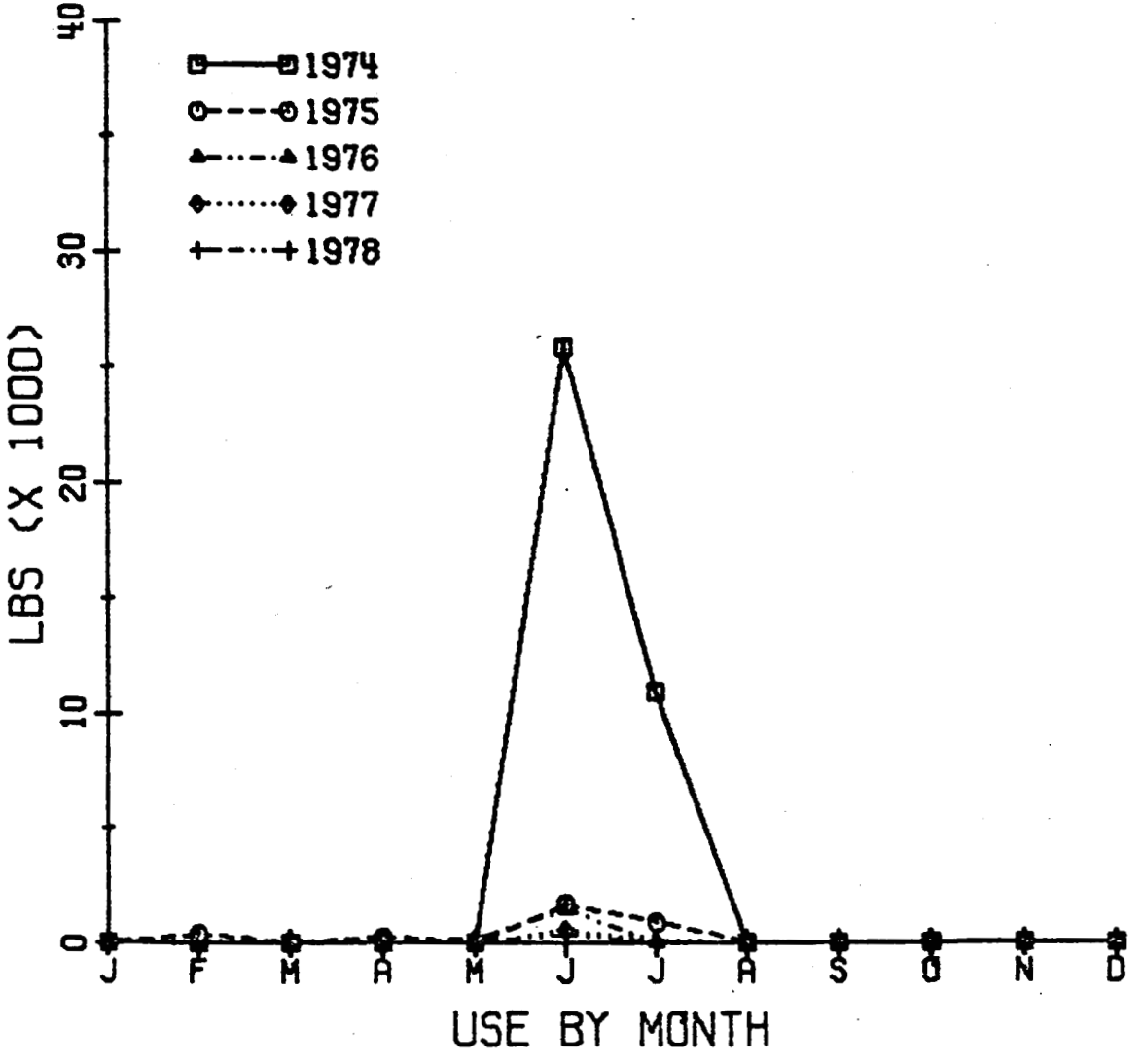


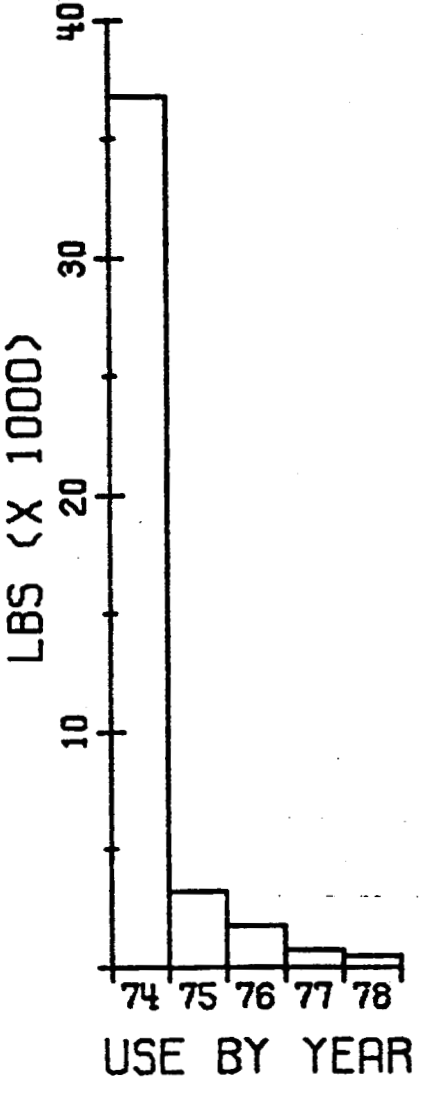
USE OF MCPA (OTHERS) IN BUTTE COUNTY



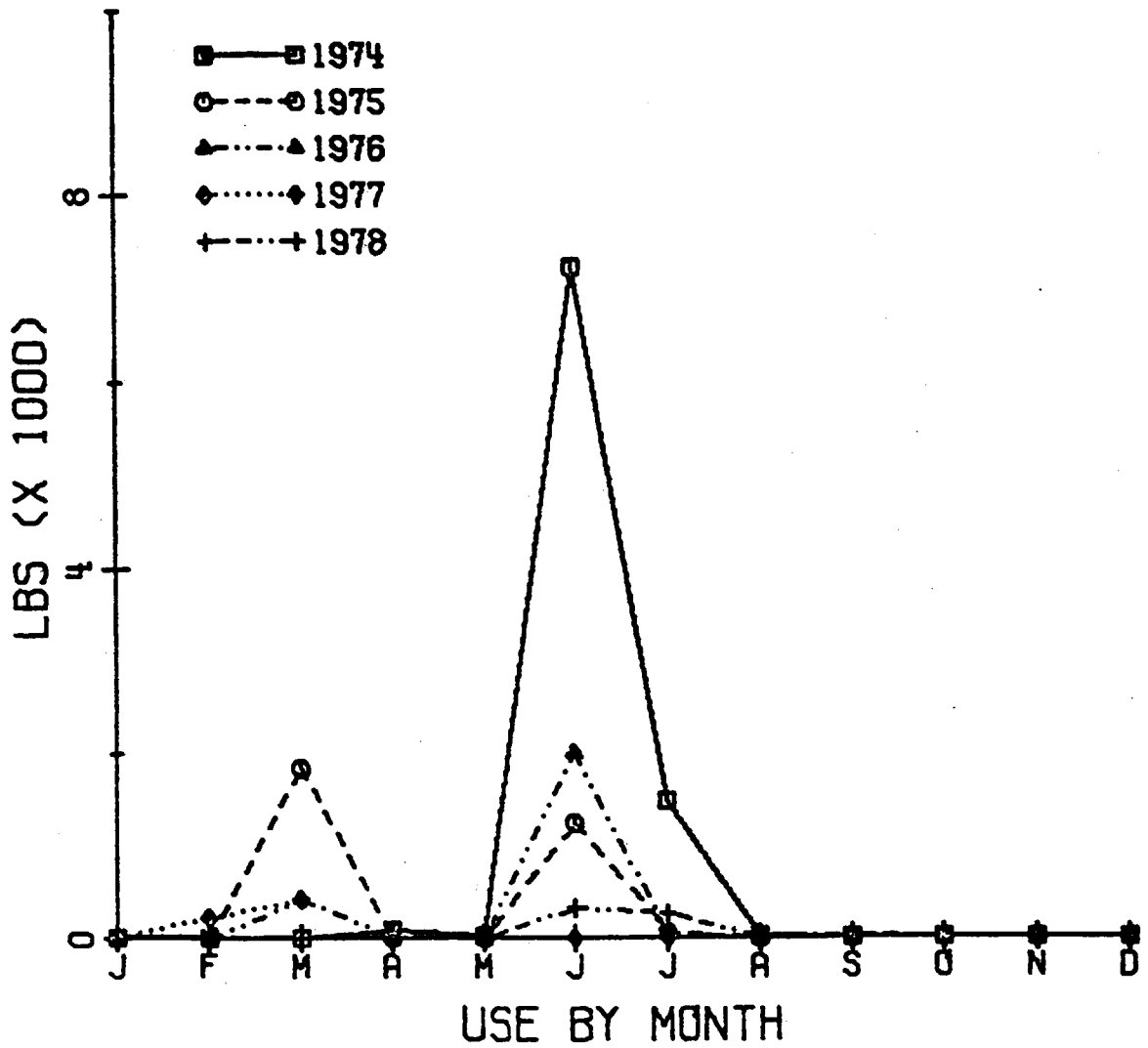


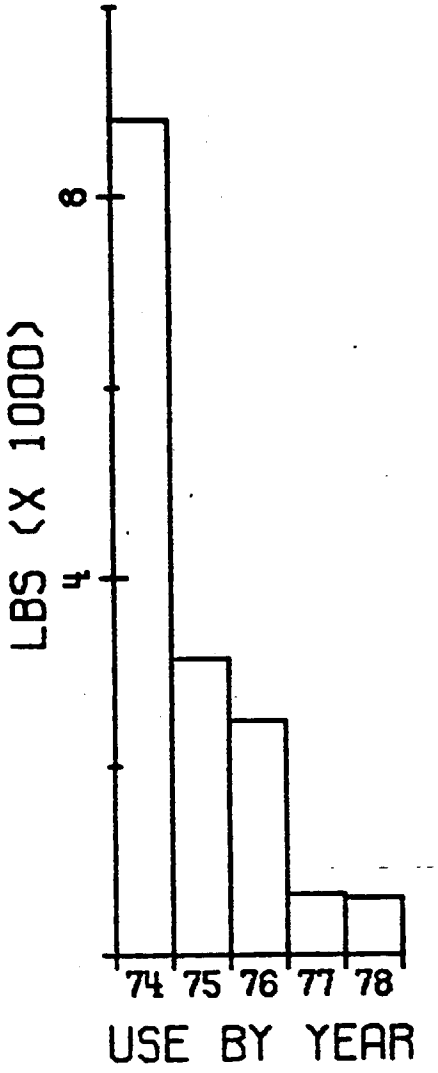
USE OF MCPA (OTHERS) IN COLUSA COUNTY



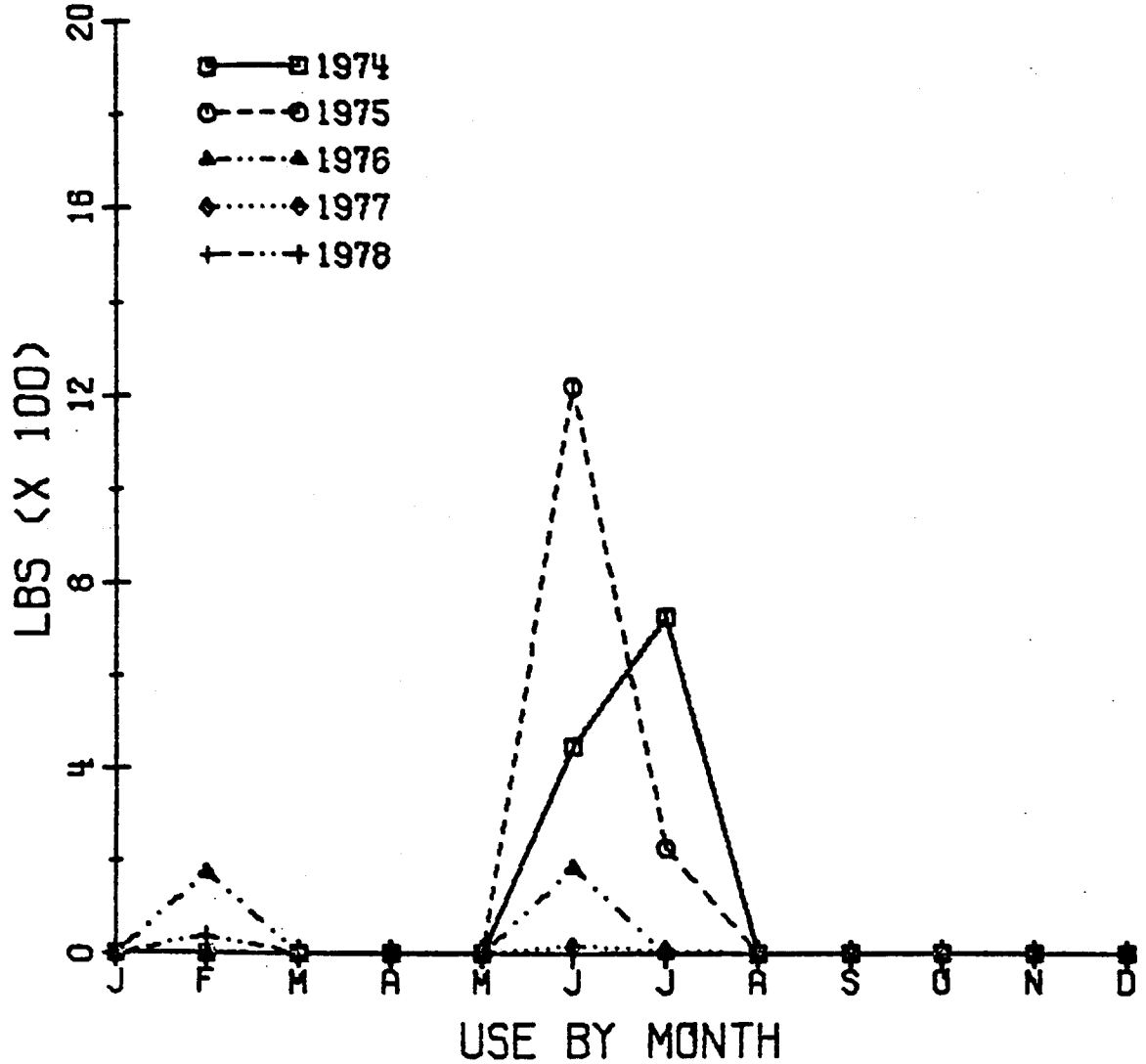


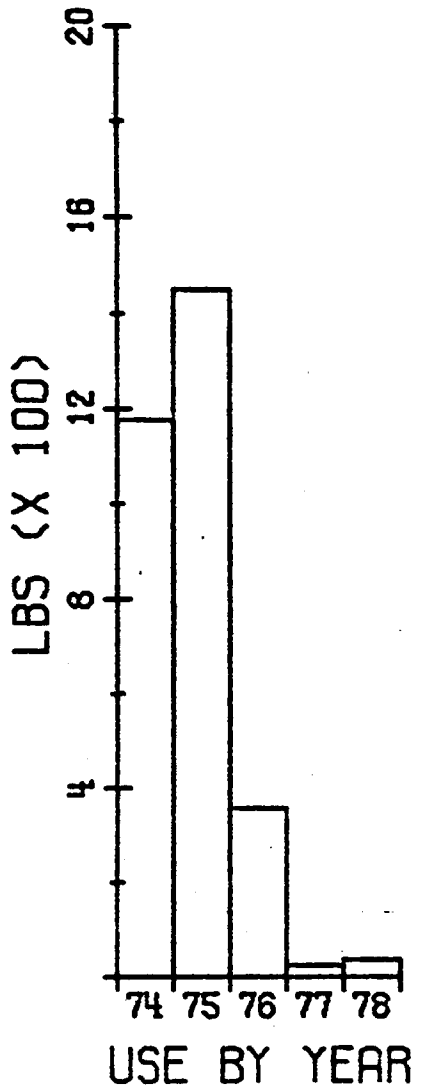
USE OF MCPA (OTHERS) IN GLENN COUNTY

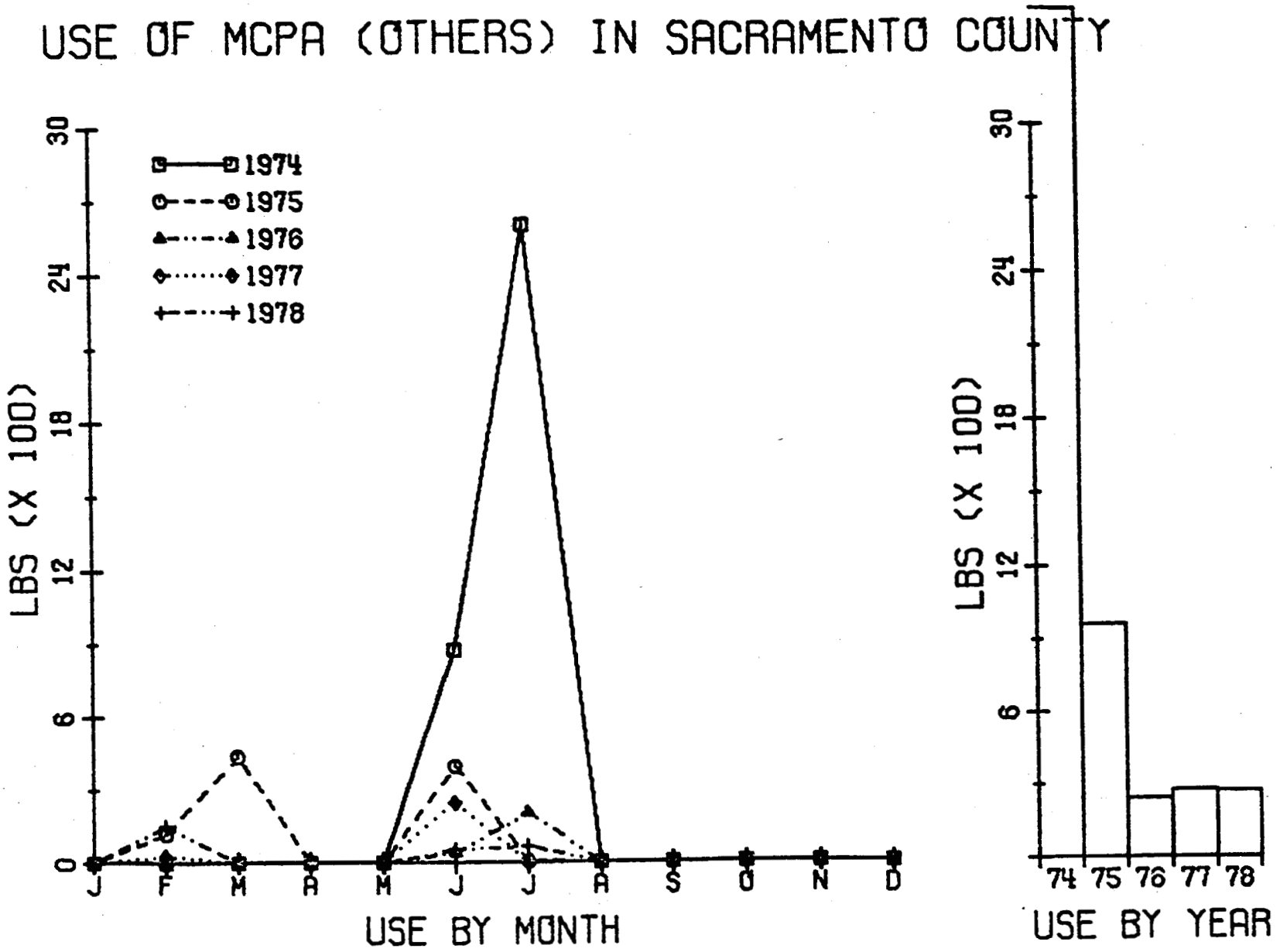




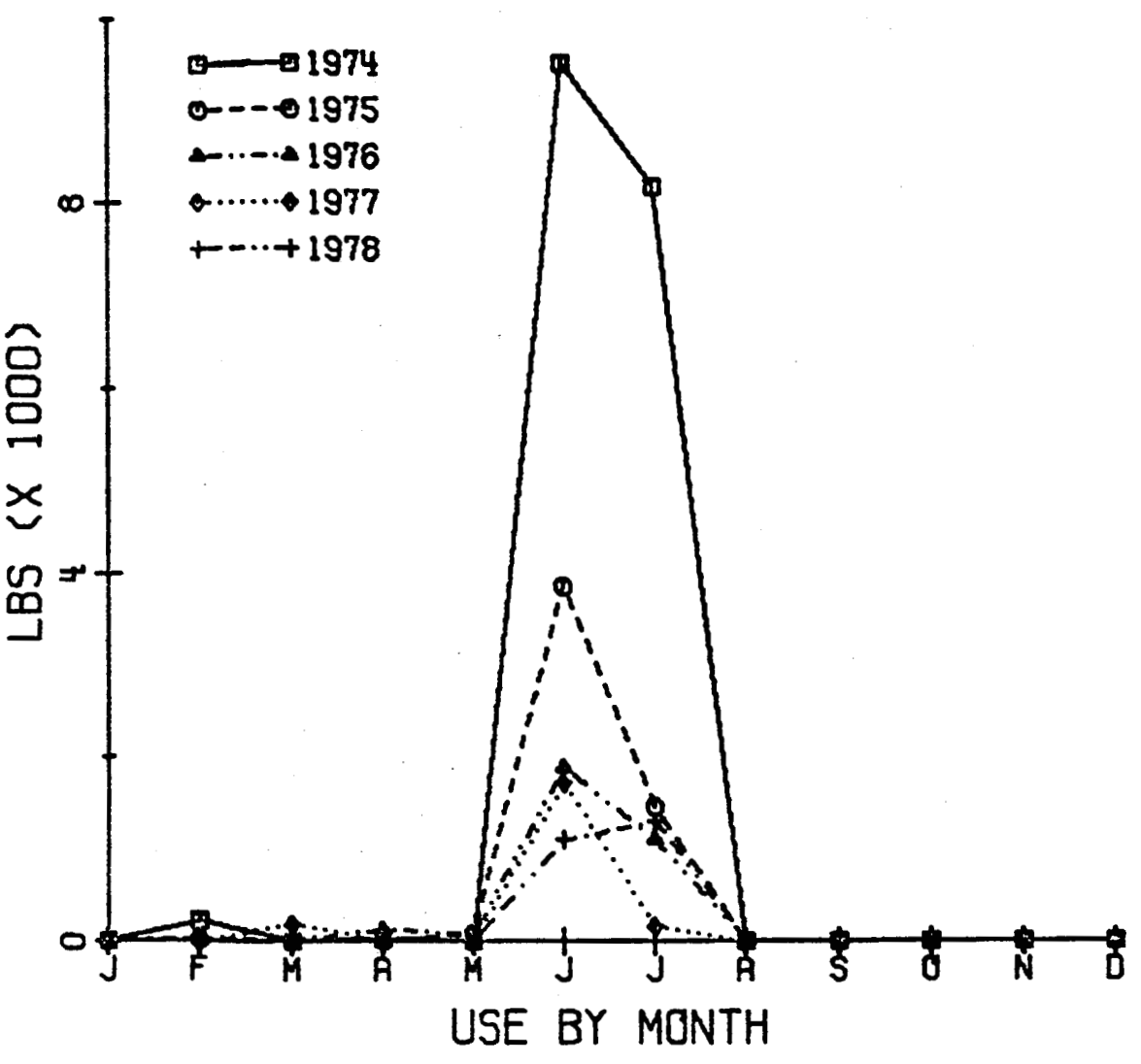
USE OF MCPA (OTHERS) IN PLACER COUNTY

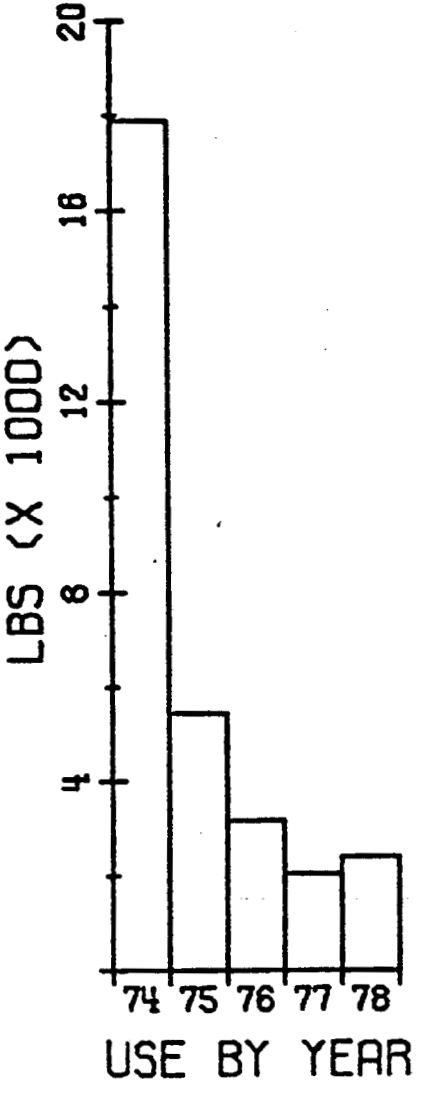




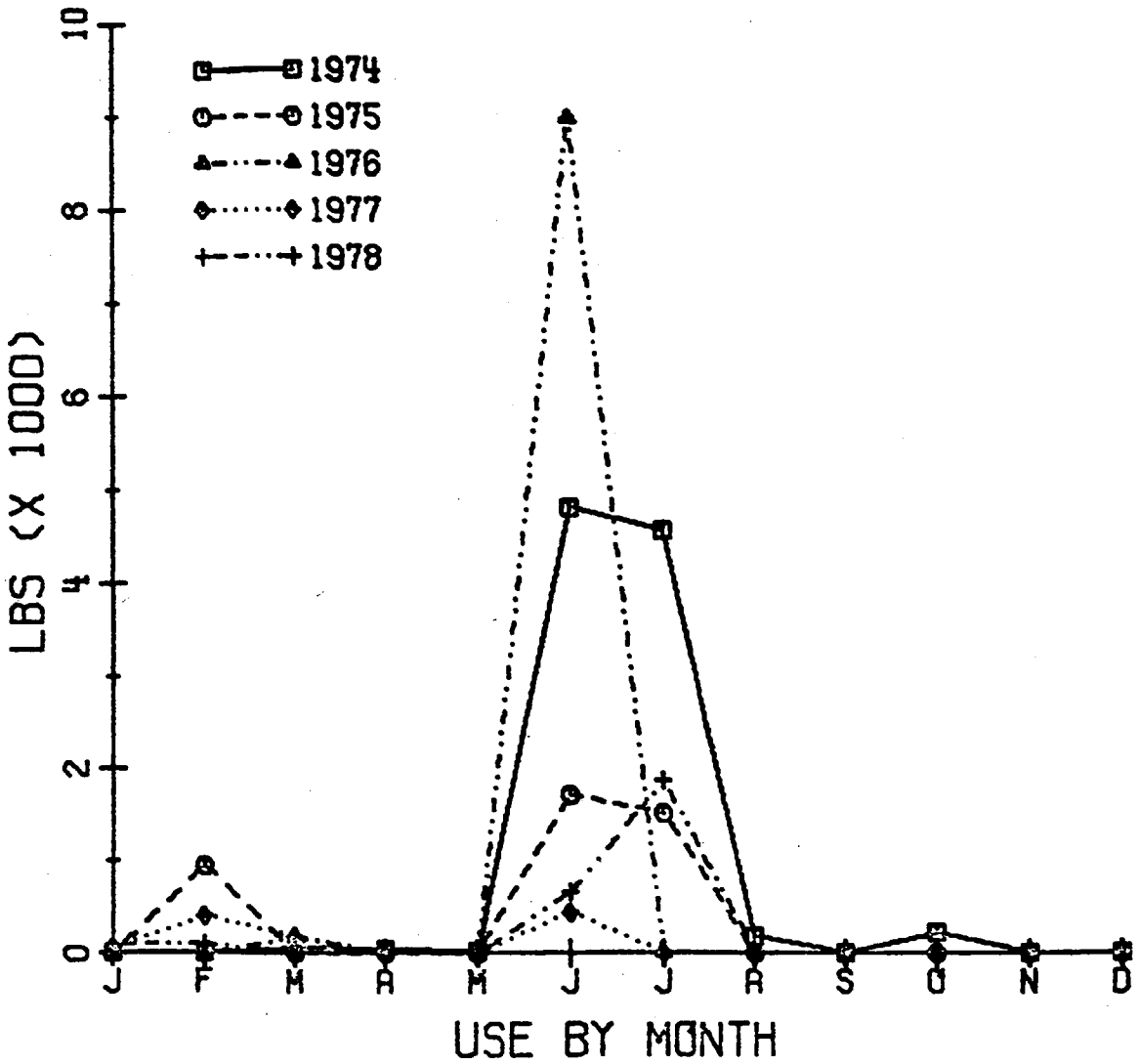

USE OF MCPA (OTHERS) IN SACRAMENTO COUNTY
1974
1975
1976
1977
1978
LBS (X 100)
0
6
12
18
24
30
J
F
M
A
M
J
J
A
S
O
N
D
USE BY MONTH
74
75
76
77
78
USE BY YEAR

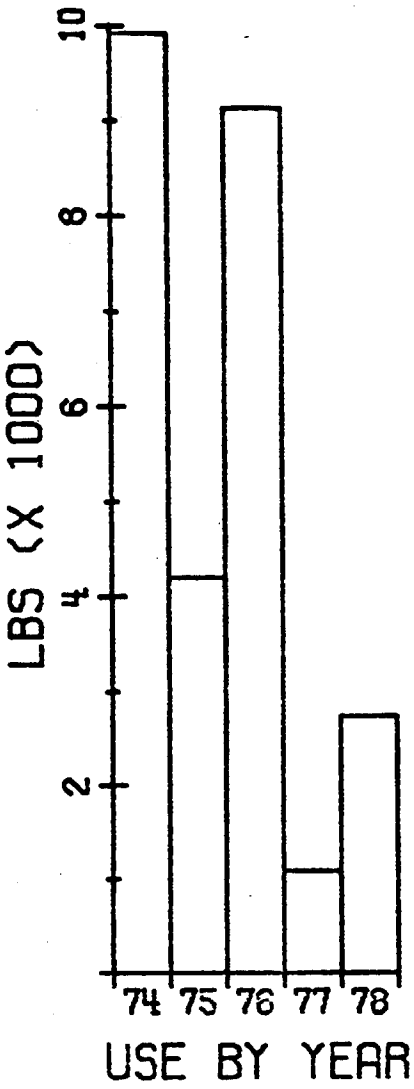
USE OF MCPA (OTHERS) IN SUTTER COUNTY



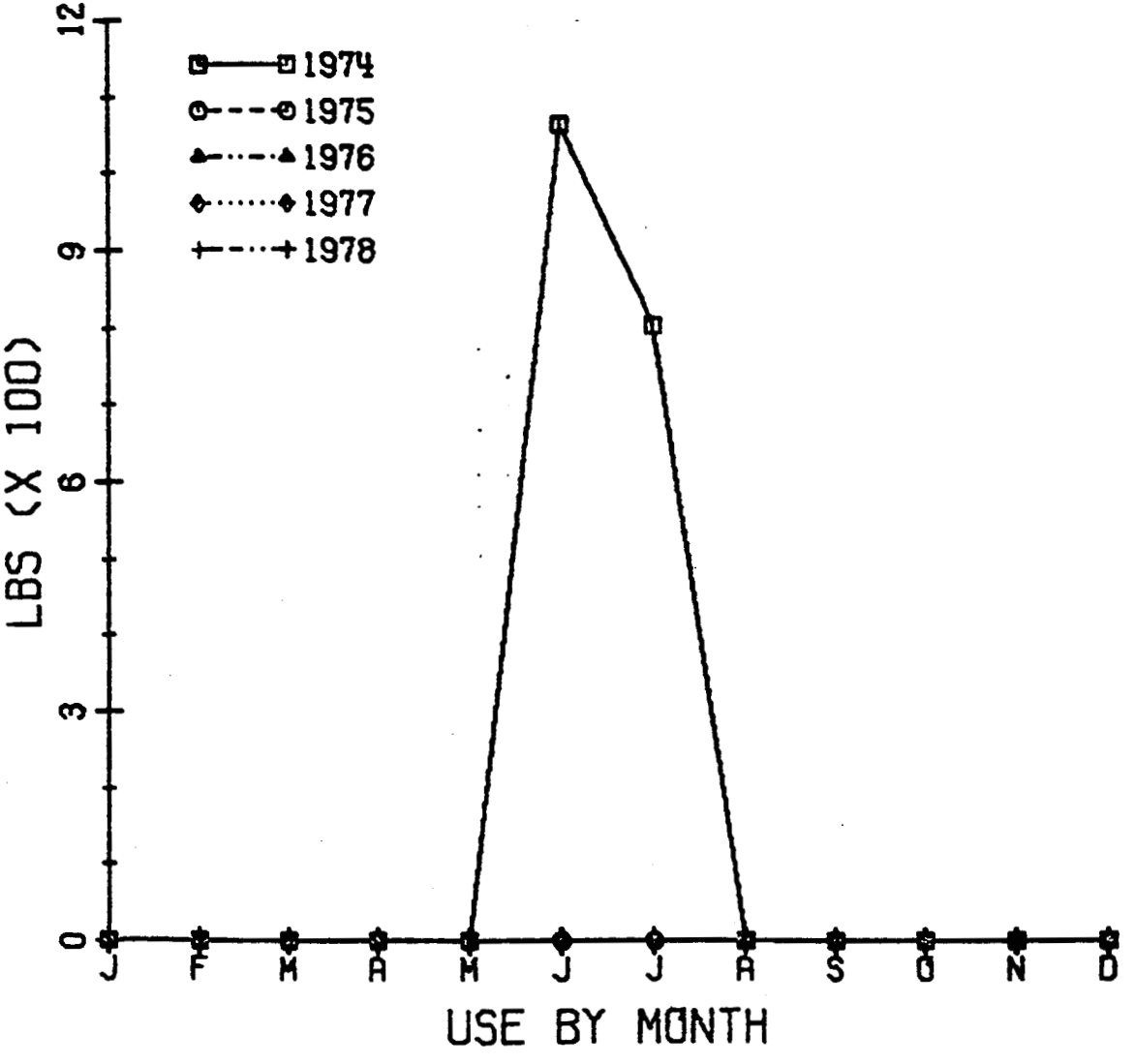


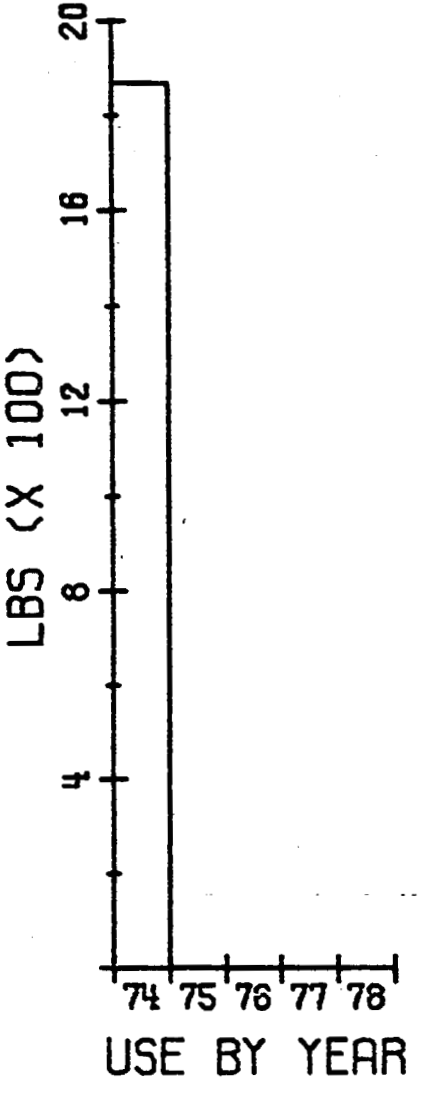
USE OF MCPA (OTHERS) IN YOLO COUNTY





USE OF MCPA (OTHERS) IN YUBA COUNTY





Appendix IIA

TOTAL POUNDS OF MCPA AMINE SALT USED IN EIGHT CALIFORNIA COUNTIES BY MONTH AND YEAR, 1974 - 78

Appendix IIB

TOTAL POUNDS OF ALL OTHER MCPA DERIVATIVES USED IN EIGHT CALIFORNIA COUNTIES BY MONTH AND YEAR, 1974 - 78

TOTAL POUNDS OF

MCPA (AMINES)

00784 00786

USED IN COUNTIES OF CALIFORNIA

BY MONTHS OF 1974

MONTH / COUNTY	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	TOTAL
BUTTE	409	775	306	5	0	31240	13782	0	0	0	0	0	46517
COLUSA	204	0	0	0	224	32654	13316	100	0	0	0	0	46498
GLENN	675	171	144	0	196	21753	24519	22	0	0	0	0	47480
PLACER	0	244	23	0	0	674	1672	0	0	0	0	0	2613
SACRAMENTO	98	85	0	0	0	1865	2065	0	0	0	0	0	4113
SUTTER	229	366	98	20	0	18478	8649	0	0	0	0	0	27840
YOLO	308	413	456	211	0	2807	3570	0	0	0	0	0	7765
YUBA	0	0	0	0	0	4282	2391	98	0	0	0	0	6772
TOTAL	1922	2055	1026	236	420	113754	69964	220	0	0	0	0	189598

TOTAL POUNDS OF

MCPA (AMINES)

00784 00786

USED IN COUNTIES OF CALIFORNIA

BY MONTHS OF 1975

MONTH / COUNTY	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	TOTAL
BUTTE	0	53	277	7	0	39185	21747	0	174	0	0	0	61444
COLUSA	19	331	0	0	161	65184	14660	45	0	0	0	0	80401
GLENN	0	630	257	81	7	52104	9272	0	10	20	0	0	62381
PLACER	0	0	0	122	0	2997	3465	693	0	0	0	0	7278
SACRAMENTO	0	18	0	280	0	8247	9503	2252	0	0	0	0	20301
SUTTER	0	0	50	289	1202	46340	15000	88	0	0	0	0	62970
YOLO	0	180	0	37	0	8769	14376	786	0	0	0	0	24148
YUBA	0	0	0	0	0	7273	3888	93	0	0	5	0	11259
TOTAL	19	1212	584	817	1371	230100	91911	3958	184	20	5	0	330181

TOTAL POUNDS OF

MCPA (AMINES)

00784 00786

USED IN COUNTIES OF CALIFORNIA

BY MONTHS OF 1976

MONTH / COUNTY	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	TOTAL
BUTTE	712	263	1095	0	172	58504	6201	0	0	0	0	0	66947
COLUSA	68	0	66	223	1510	108499	5294	0	0	0	0	0	115660
GLENN	0	11	1461	124	305	31715	2345	209	0	0	0	0	36171
PLACER	0	0	0	0	91	3378	2088	75	0	0	0	0	5632
SACRAMENTO	0	64	12	0	37	4541	1757	0	0	0	0	490	6903
SUTTER	73	18	19	38	673	37674	7374	17	0	0	0	83	45970
YOLO	0	113	1195	1073	45	11690	2546	0	0	0	0	217	16880
YUBA	25	18	67	0	0	6949	1976	0	0	0	0	0	9035
TOTAL	878	486	3916	1459	2833	262950	29582	301	0	0	0	790	303198

TOTAL POUNDS OF

MCPA (AMINES)

00784 00786

USED IN COUNTIES OF CALIFORNIA

BY MONTHS OF 1977

MONTH / COUNTY	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	TOTAL
BUTTE	7	929	1589	816	23	51504	1193	0	0	0	0	62	56124
COLUSA	0	1708	1428	539	341	140943	3790	60	0	29	0	103	148941
GLENN	0	280	2174	94	45	103940	709	0	0	0	0	0	107242
PLACER	0	0	813	0	0	3080	1099	0	0	0	0	0	4992
SACRAMENTO	695	1001	1409	221	83	2836	1512	0	0	0	0	96	7854
SUTTER	0	296	1792	127	18	21583	2776	179	0	0	0	450	27220
YOLO	59	1088	1331	158	91	9541	810	0	0	0	0	37	13114
YUBA	0	72	917	151	0	8188	416	0	0	0	0	0	9745
TOTAL	761	5374	11453	2107	600	341616	12305	239	0	29	0	748	375233

TOTAL POUNDS OF

MCPA (AMINES)

00784 00786

USED IN COUNTIES OF CALIFORNIA

BY MONTHS OF 1978

MONTH / COUNTY	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	TOTAL
BUTTE	269 0	956 0	696 698	28	0 0	43276 5359	32954 27594	0 0	0 0	0 0	0	0 0	78273 33679
COLUSA	1712 0	2778 0	59 59	0	562 562	70233 16680	35513 19603	770 0	0 0	0 0	0	0 0	111627 36904
GLENN	991 0	720 0	430 430	39	0 0	31111 26445	32989 6545	0 7	96 88	0 0	0	0 0	66376 33554
PLACER	337 0	992 0	0 0	0	0 0	1407 845	8411 7565	0 0	74 74	0 0	0	0 0	11221 8484
SACRAMENTO	135 0	795 0	483 483	0	114 104	12909 2024	8745 6721	0 0	0 0	0 0	0	0 0	23121 9332
SUTTER	326 0	793 214	548 334	0	87 87	24221 1632	34058 37425	126 126	0 0	0 0	0	0 0	65159 39818
YOLO	258 0	735 0	239 247	43	21 13	1759 5417	13938 8521	0 0	0 0	0 0	0	0 0	16993 14241
YUBA	660 0	369 0	92 92	0	0 0	4681 303	8243 7940	101 101	0 0	0 0	0	0 0	14147 8436
TOTAL	0	214	2343	109	765	58706	121916	234	162	0	0	0	184448

TOTAL POUNDS OF

MCPA (OTHERS)

00785 00787 00788

USED IN COUNTIES OF CALIFORNIA

BY MONTHS OF 1974

MONTH / COUNTY	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	TOTAL
BUTTE	0	0	0	1	0	4409	6584	0	0	0	0	456	11451
COLUSA	0	0	0	0	0	25805	10986	0	0	0	0	0	36790
GLENN	0	0	0	75	14	7228	1476	17	0	0	0	0	8809
PLACER	0	0	0	0	0	448	727	0	0	0	0	0	1175
SACRAMENTO	0	0	0	0	0	874	2596	0	0	0	0	0	3471
SUTTER	0	219	0	22	0	9495	8155	0	0	0	0	0	17891
YOLO	0	0	54	46	29	4813	4582	174	0	221	0	0	9919
YUBA	0	0	0	0	0	1064	805	0	0	0	0	0	1869
TOTAL	0	219	54	144	43	54136	35911	191	0	221	0	456	91374

TOTAL POUNDS OF

MCPA (OTHERS)

00785 00787 00788

USED IN COUNTIES OF CALIFORNIA

BY MONTHS OF 1975

MONTH / COUNTY	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	TOTAL
BUTTE	9	679	0	0	4	1309	130	0	0	0	0	0	2132
COLUSA	0	404	0	269	0	1649	904	0	0	0	0	0	3227
GLENN	0	0	1843	1	0	1232	54	0	0	0	0	0	3130
PLACER	0	0	0	0	0	1222	229	0	0	0	0	0	1452
SACRAMENTO	0	120	436	0	0	395	7	0	0	0	0	0	959
SUTTER	0	25	0	0	73	3863	1466	0	0	0	0	0	5426
YOLO	0	948	0	0	0	1720	1522	0	0	0	0	0	4191
YUBA	0	0	0	0	0	0	0	0	0	0	0	0	0
TOTAL	9	2177	2279	270	77	11391	4313	0	0	0	0	0	20517

TOTAL POUNDS OF

MCPA (OTHERS)

00785 00787 00788

USED IN COUNTIES OF CALIFORNIA

BY MONTHS OF 1976

MONTH / COUNTY	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	TOTAL
BUTTE	4	0	25	0	0	737	46	0	0	0	0	0	813
COLUSA	0	0	112	0	185	1433	0	0	0	0	0	0	1729
GLENN	23	0	414	0	0	2005	35	0	0	0	0	0	2477
PLACER	0	172	0	0	0	185	0	0	0	0	0	0	356
SACRAMENTO	0	0	0	0	0	40	202	0	0	0	0	0	241
SUTTER	0	0	0	129	62	1887	1098	0	0	0	0	0	3176
YOLO	0	0	155	0	0	8982	0	0	0	0	0	0	9137
YUBA	0	0	0	0	0	0	0	0	0	0	0	0	0
TOTAL	28	172	706	129	247	15269	1381	0	0	0	0	0	17931

TOTAL POUNDS OF

NCPA (OTHERS)

00785 00787 00788

USED IN COUNTIES OF CALIFORNIA

BY MONTHS OF 1977

MONTH / COUNTY	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	TOTAL
BUTTE	0	0	0	0	0	48	0	0	0	0	0	0	48
COLUSA	3	62	0	0	0	546	81	0	0	0	0	33	726
GLENN	0	222	420	0	0	6	0	0	0	0	0	0	647
PLACER	0	0	0	0	0	17	6	0	0	0	0	0	23
SACRAMENTO	0	29	0	0	0	247	0	0	0	0	0	0	276
SUTTER	0	0	186	0	0	1713	152	0	0	0	0	0	2050
YOLO	62	401	176	0	0	444	0	0	0	0	0	0	1083
YUBA	0	0	0	0	0	0	0	0	0	0	0	0	0
TOTAL	66	715	781	0	0	3020	240	0	0	0	0	33	4854

TOTAL POUNDS OF

MCPA (OTHERS)

00785 00787 00788

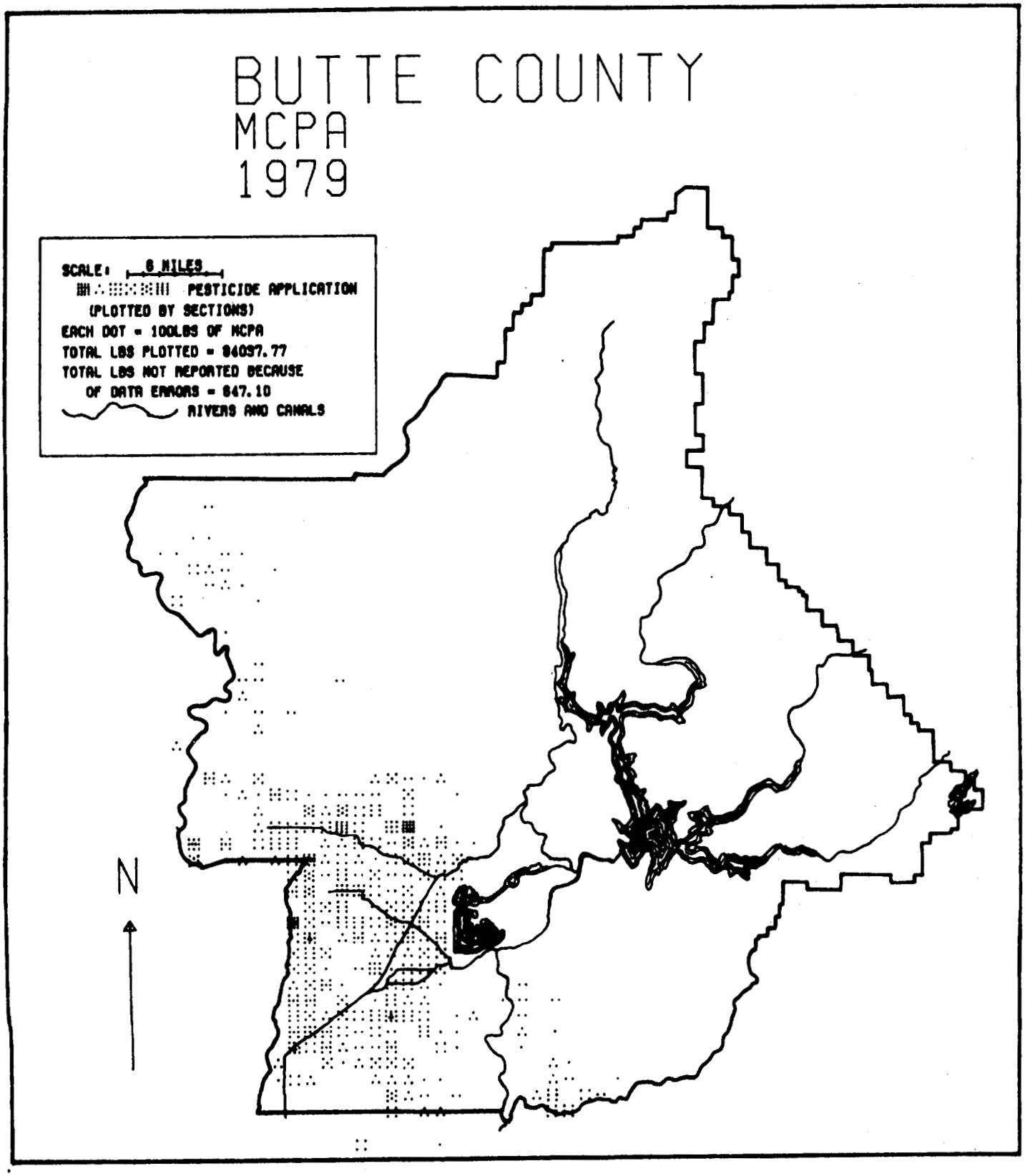
USED IN COUNTIES OF CALIFORNIA

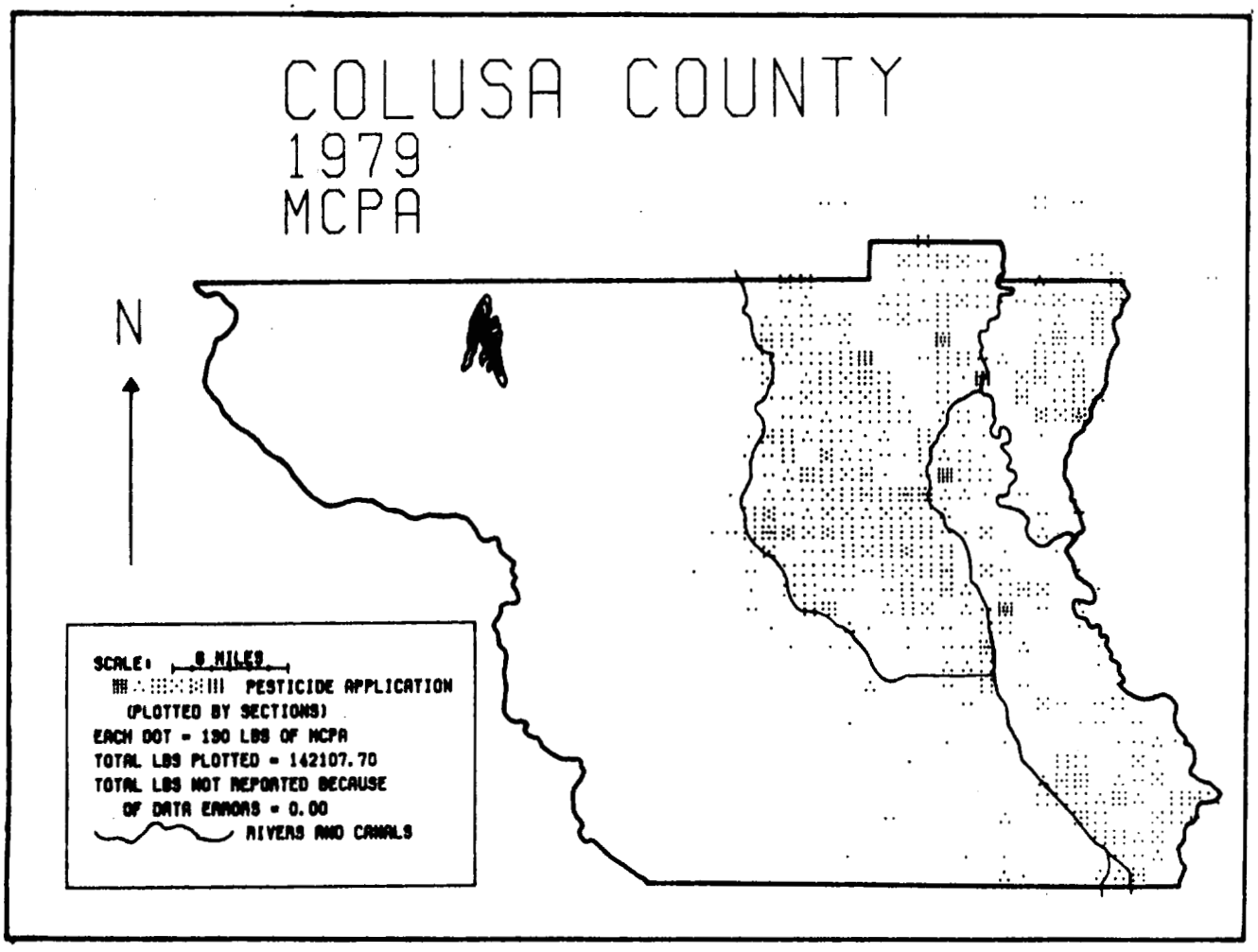
BY MONTHS OF 1978

MONTH / COUNTY	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	TOTAL
BUTTE	0 0	0 0	0 0	0	0 0	67 0	0 0	0 0	0 0	0 0	0	0 0	67 0
COLUSA	0 0	0 0	0 0	0	0 0	351 0	0 0	0 0	0 0	0 0	0	0 0	468 0
GLENN	0 0	0 0	0 0	0	0 0	321 198	263 84	0 0	20 0	0 0	0	0 0	604 282
PLACER	0 0	37 0	0 0	0	0 0	0 0	0 0	0 0	0 0	0 0	0	0 0	37 0
SACRAMENTO	0 0	150 0	0 0	0	0 0	54 0	66 66	0 0	0 0	0 0	0	0 0	270 66
SUTTER	0 0	0 0	0 0	0	0 0	1095 31	1299 1268	0 0	0 0	0 0	0	0 0	2394 1299
YOLO	89 0	101 0	0 0	0	0 0	670 888	1875 987	0 0	0 0	0 0	0	0 0	2734 1875
YUBA	0 0	0 0	0 0	0	0 0	0 0	0 0	0 0	0 0	0 0	0	0 0	0 0
TOTAL	0	0	0	0	0	1116	2405	0	0	0	0	0	3522

Appendix III

LOCATION OF MCPA APPLICATIONS IN EIGHT CALIFORNIA COUNTIES, 1979


BUTTE COUNTY
MCPA
1979
SCALE: 8 MILES
PESTICIDE APPLICATION
(PLOTTED BY SECTIONS)
EACH DOT = 100LBS OF MCPA
TOTAL LBS PLOTTED = 84097.77
TOTAL LBS NOT REPORTED BECAUSE
OF DATA ERRORS = 847.10
RIVERS AND CANALS
N


COLUSA COUNTY
1979
MCPA
N
SCALE: 8 MILES
PESTICIDE APPLICATION
(PLOTTED BY SECTIONS)
EACH DOT = 190 LBS OF MCPA
TOTAL LBS PLOTTED = 142107.70
TOTAL LBS NOT REPORTED BECAUSE
OF DATA ERRORS = 0.00
RIVERS AND CANALS

GLENN COUNTY
MCPA
1979

SCALE: 6 MILES

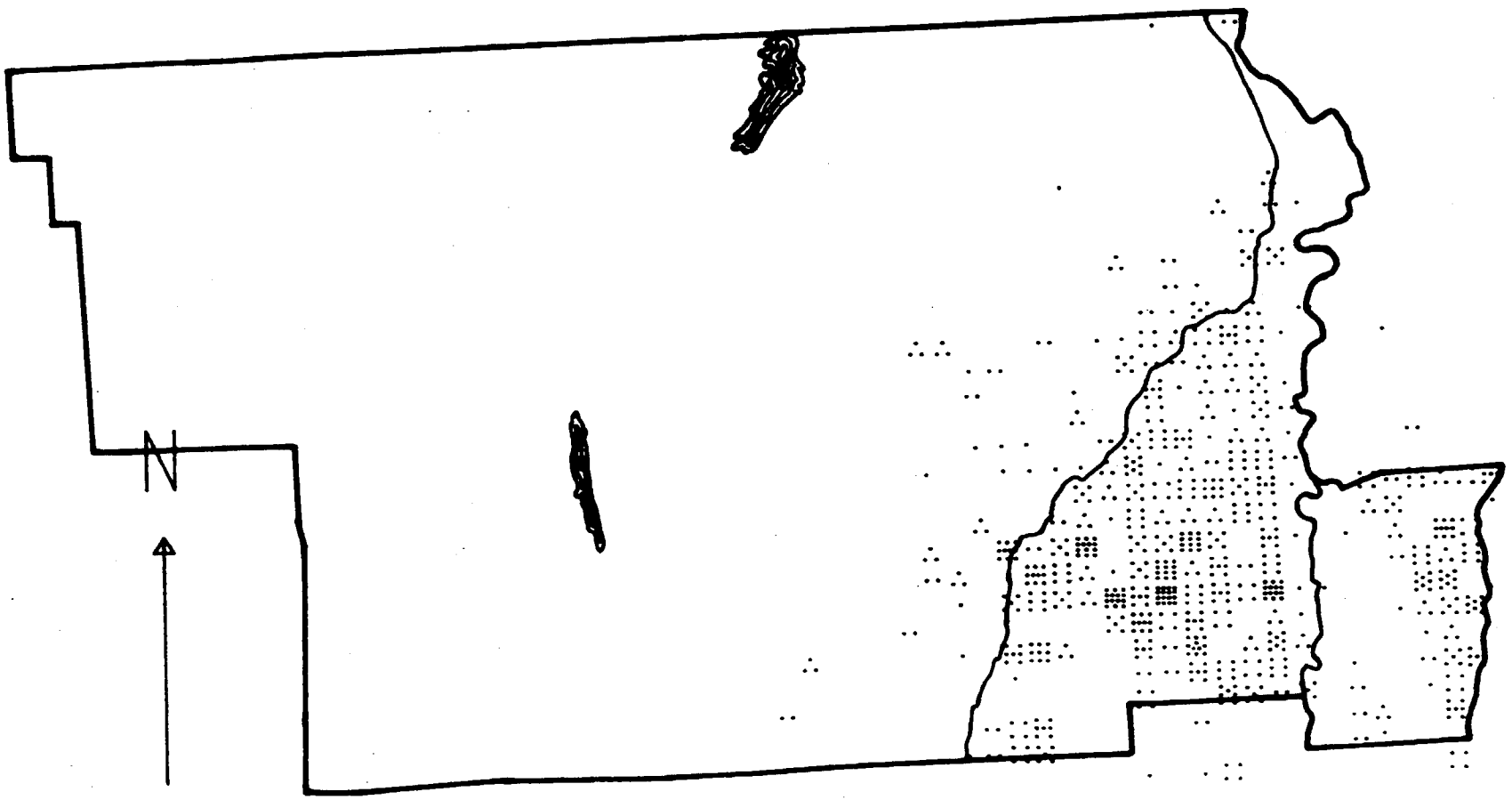
PESTICIDE APPLICATION
(PLOTTED BY SECTIONS)

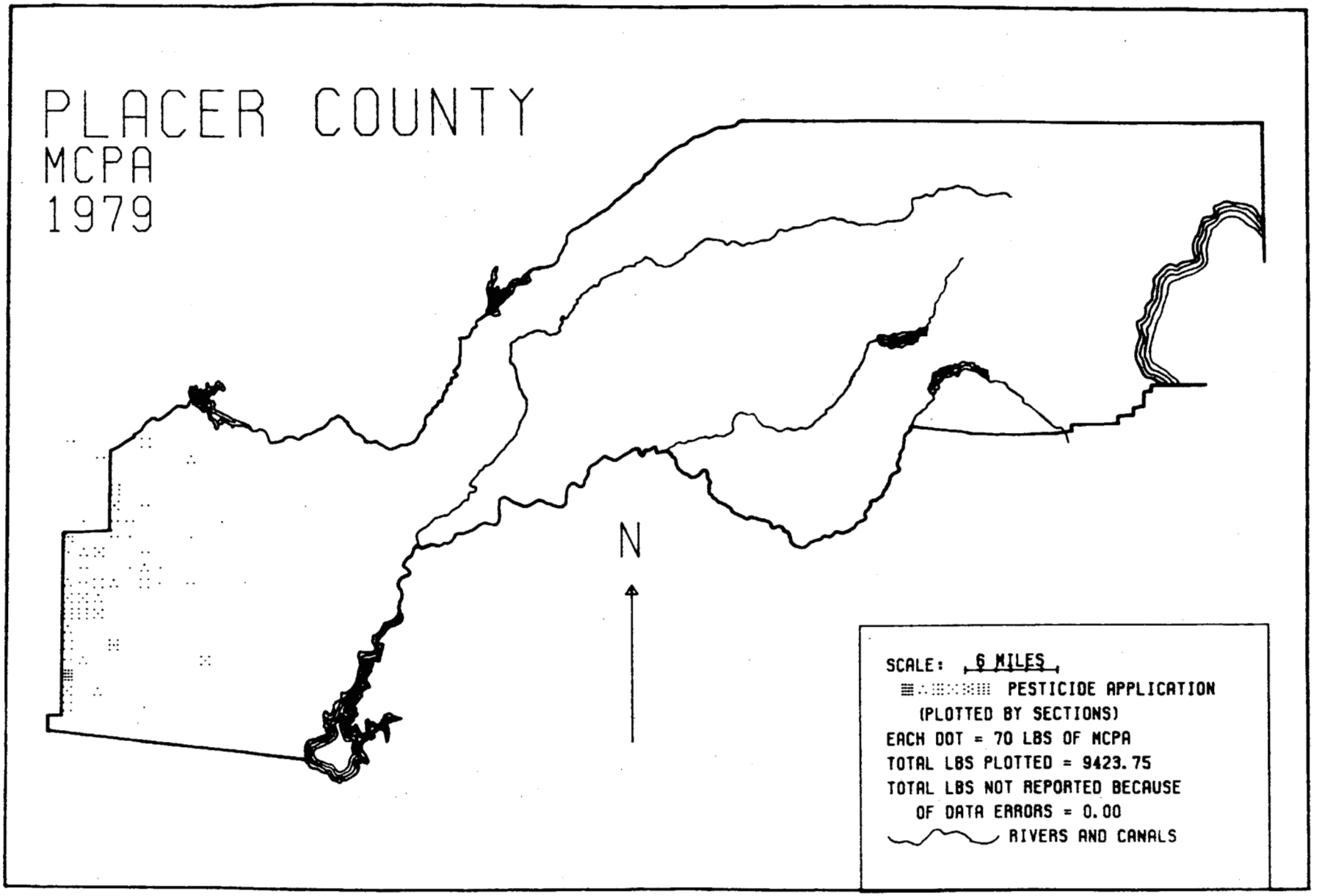
EACH DOT = 80 LBS OF MCPA

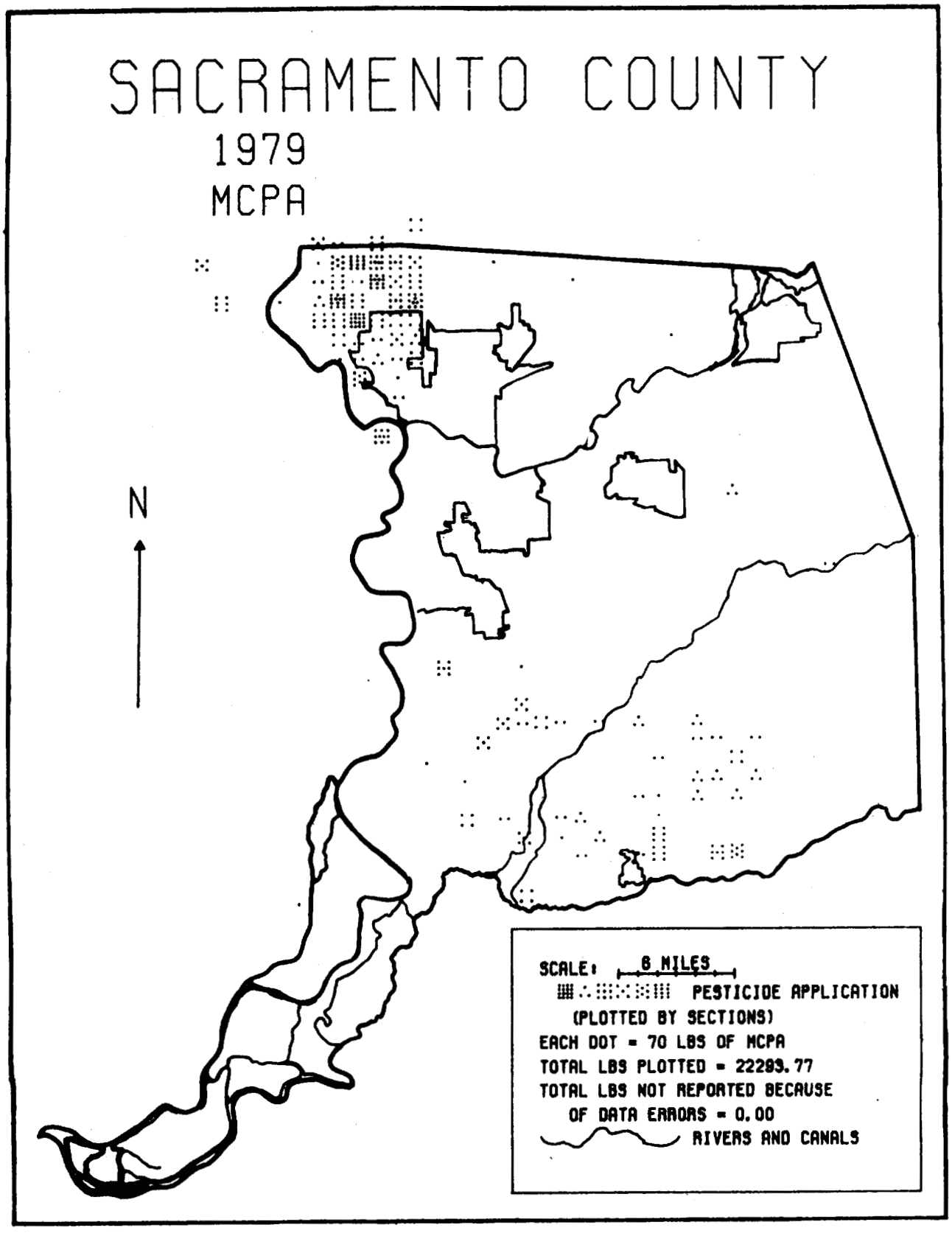
TOTAL LBS PLOTTED = 60412.48

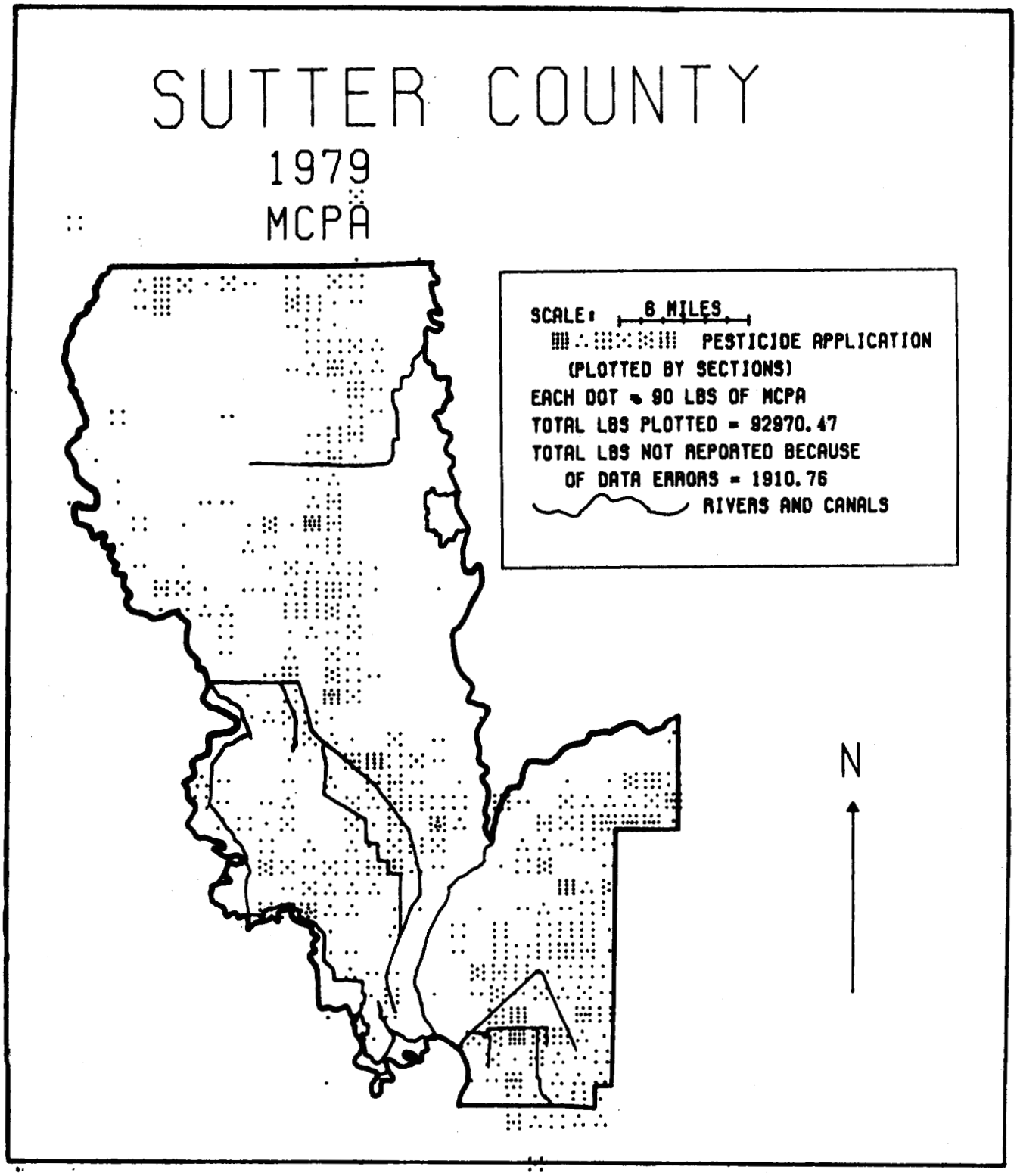
TOTAL LBS NOT REPORTED BECAUSE OF DATA ERRORS = 0.00

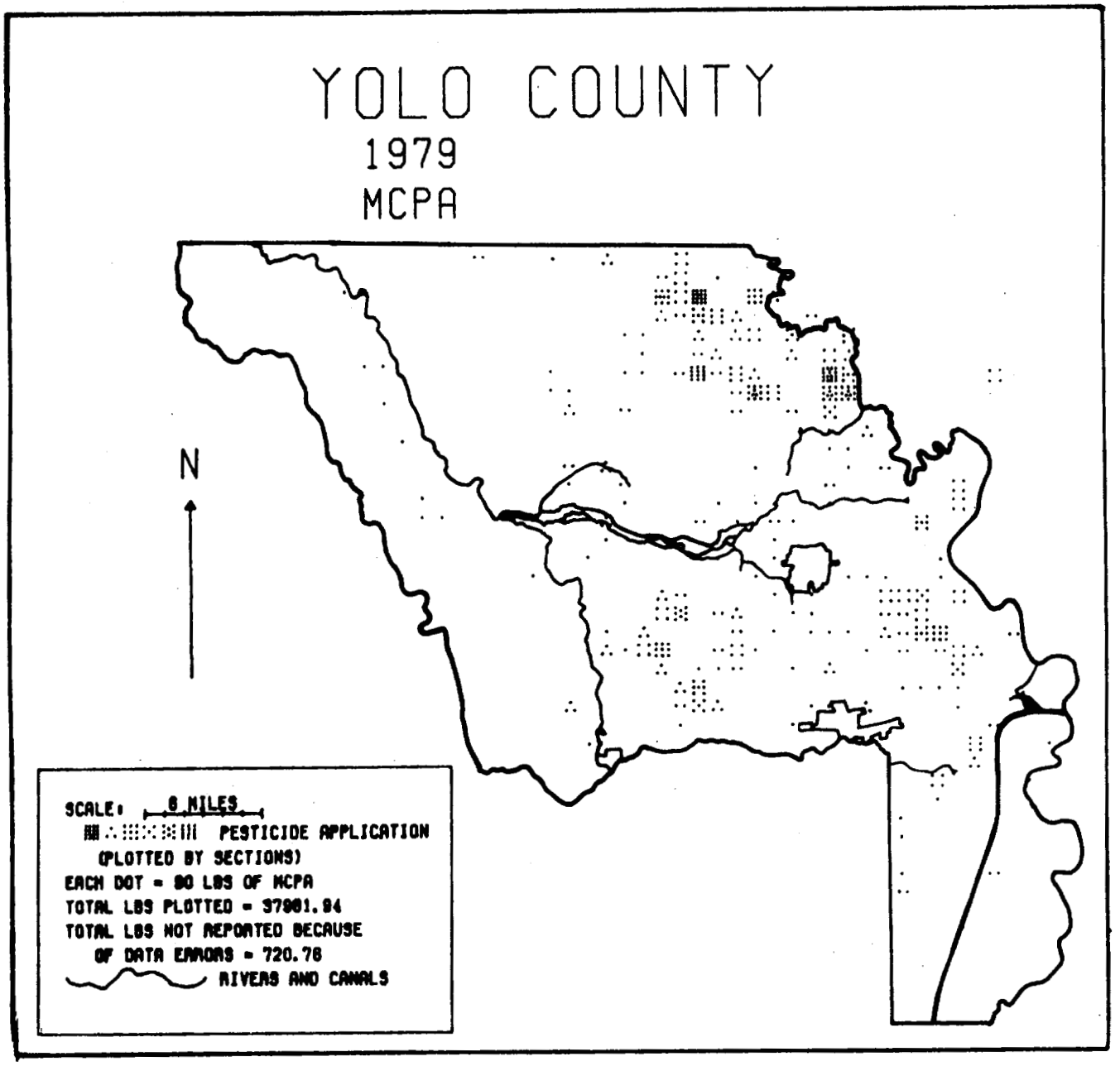
RIVERS AND CANALS

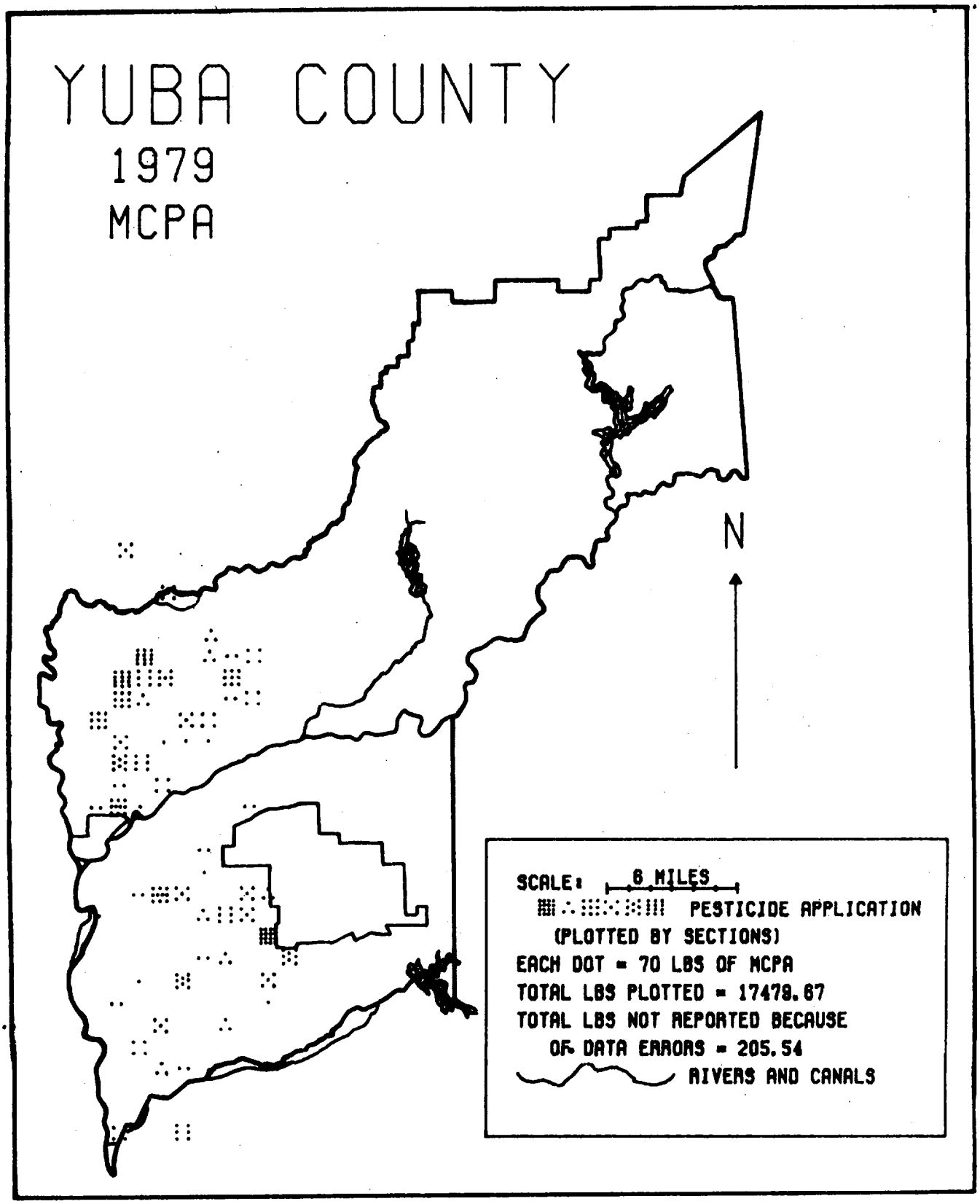



PLACER COUNTY
MCPA
1979
N
SCALE: 6 MILES
PESTICIDE APPLICATION
(PLOTTED BY SECTIONS)
EACH DOT = 70 LBS OF MCPA
TOTAL LBS PLOTTED = 9423.75
TOTAL LBS NOT REPORTED BECAUSE
OF DATA ERRORS = 0.00
RIVERS AND CANALS


SACRAMENTO COUNTY
1979
MCPA
N
SCALE: 6 MILES
PESTICIDE APPLICATION
(PLOTTED BY SECTIONS)
EACH DOT = 70 LBS OF MCPA
TOTAL LBS PLOTTED = 22283.77
TOTAL LBS NOT REPORTED BECAUSE
OF DATA ERRORS = 0.00
RIVERS AND CANALS


SUTTER COUNTY
1979
MCPA
SCALE: 6 MILES
PESTICIDE APPLICATION
(PLOTTED BY SECTIONS)
EACH DOT = 90 LBS OF MCPA
TOTAL LBS PLOTTED = 92970.47
TOTAL LBS NOT REPORTED BECAUSE
OF DATA ERRORS = 1910.76
RIVERS AND CANALS
N

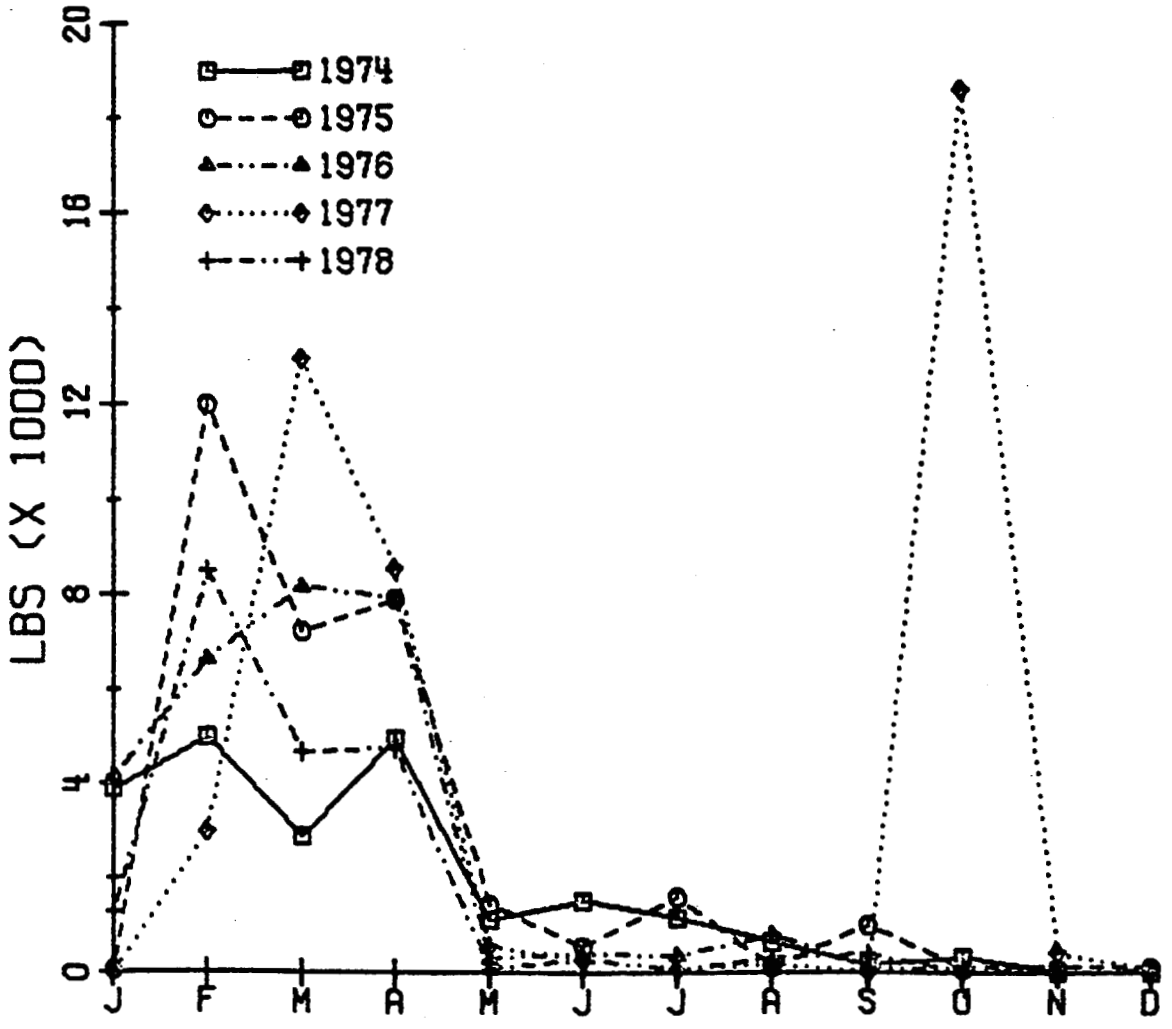

YOLO COUNTY
1979
MCPA
N
SCALE: 6 MILES
PESTICIDE APPLICATION
(PLOTTED BY SECTIONS)
EACH DOT = 80 LBS OF MCPA
TOTAL LBS PLOTTED = 37981.94
TOTAL LBS NOT REPORTED BECAUSE
OF DATA ERRORS = 720.76
RIVERS AND CANALS

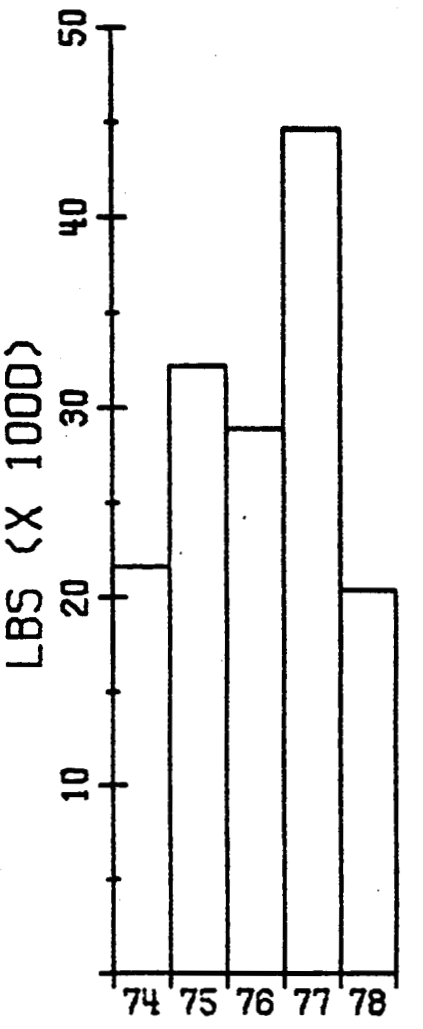

YUBA COUNTY
1979
MCPA
N
SCALE: 6 MILES
PESTICIDE APPLICATION
(PLOTTED BY SECTIONS)
EACH DOT = 70 LBS OF MCPA
TOTAL LBS PLOTTED = 17479.67
TOTAL LBS NOT REPORTED BECAUSE
OF DATA ERRORS = 205.54
RIVERS AND CANALS

Appendix IV

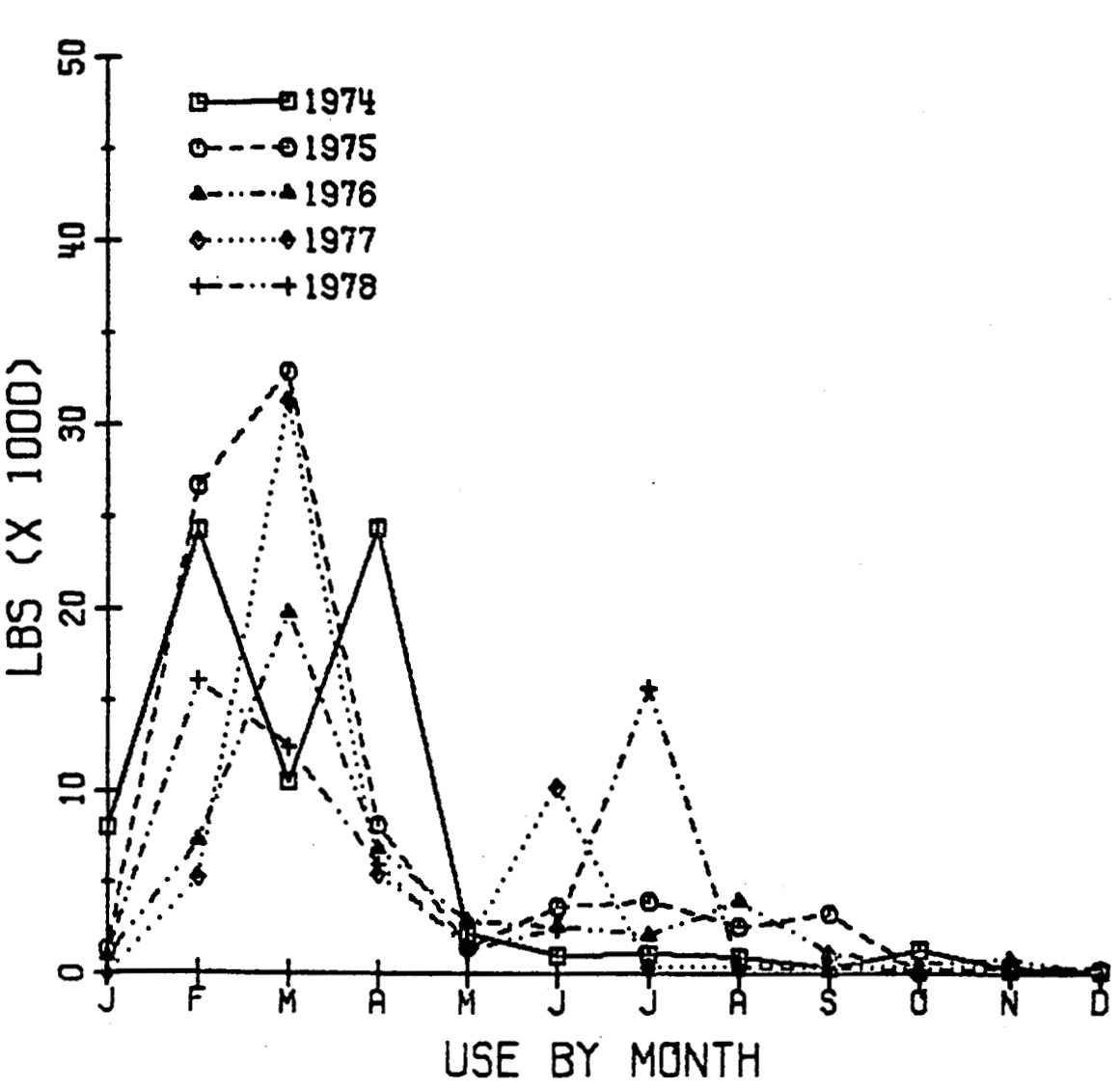
USE OF ALL FORMS OF 2,4-D IN EIGHT CALIFORNIA COUNTIES BY MONTH AND YEAR, 1974 - 78

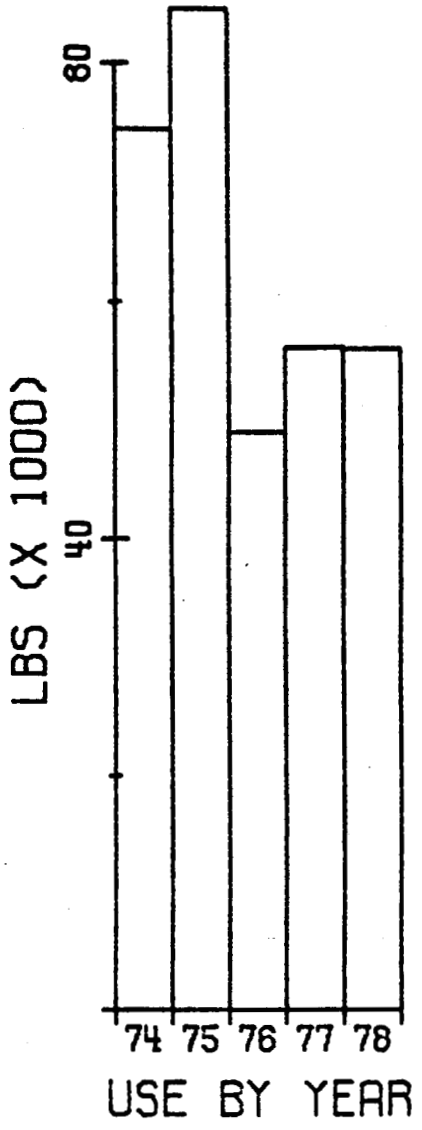
USE OF 2,4-D (ALL FORMS) IN BUTTE COUNTY



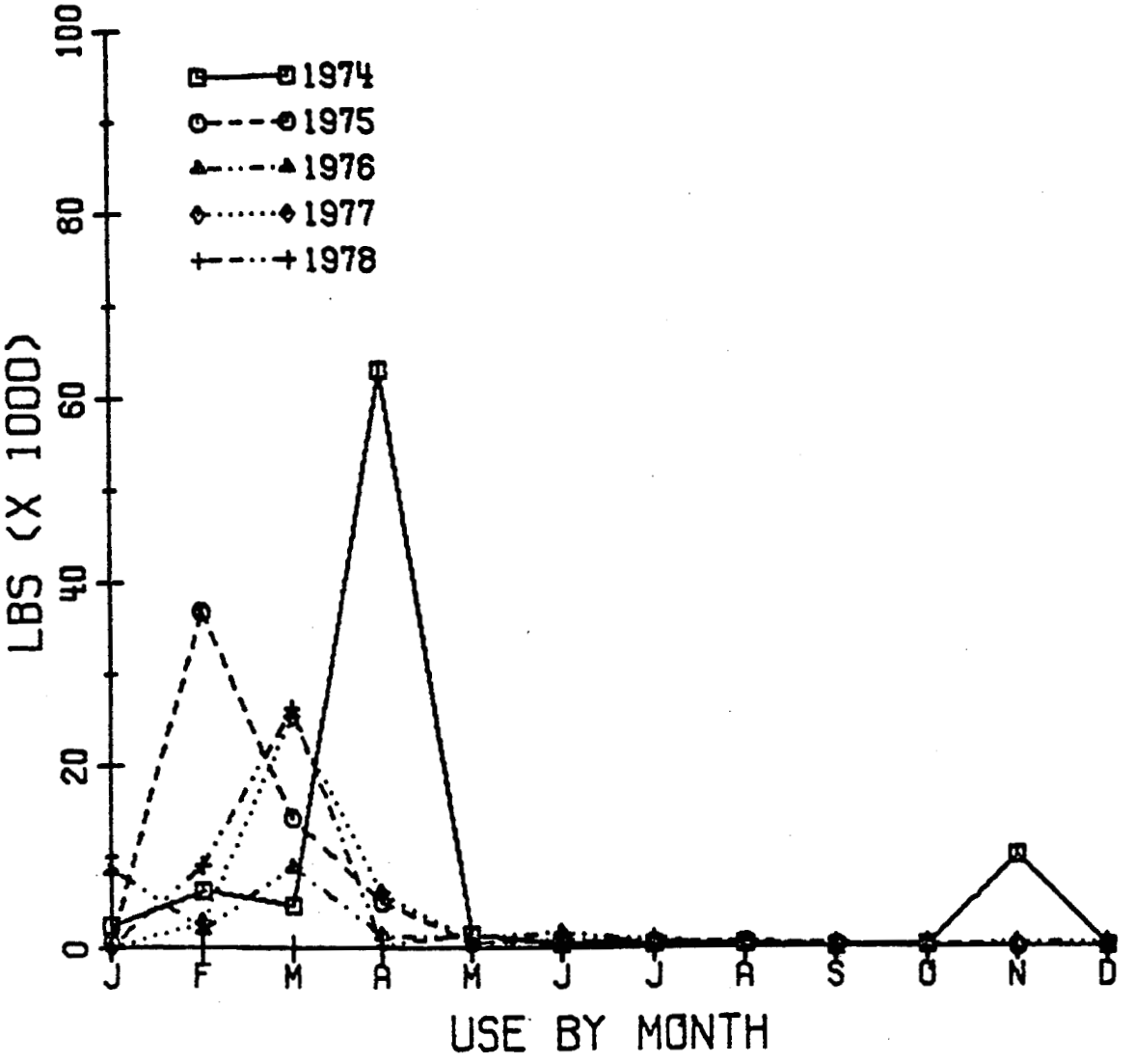


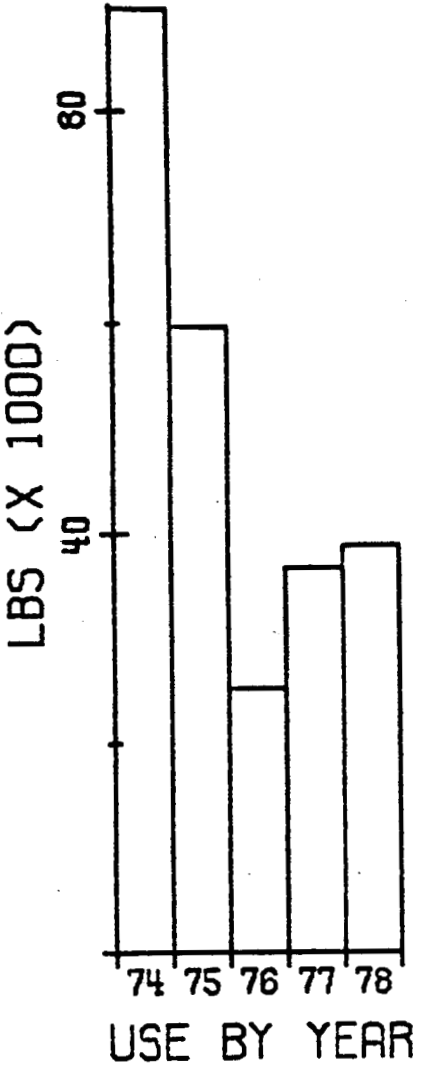
USE OF 2,4-D (ALL FORMS) IN COLUSA COUNTY



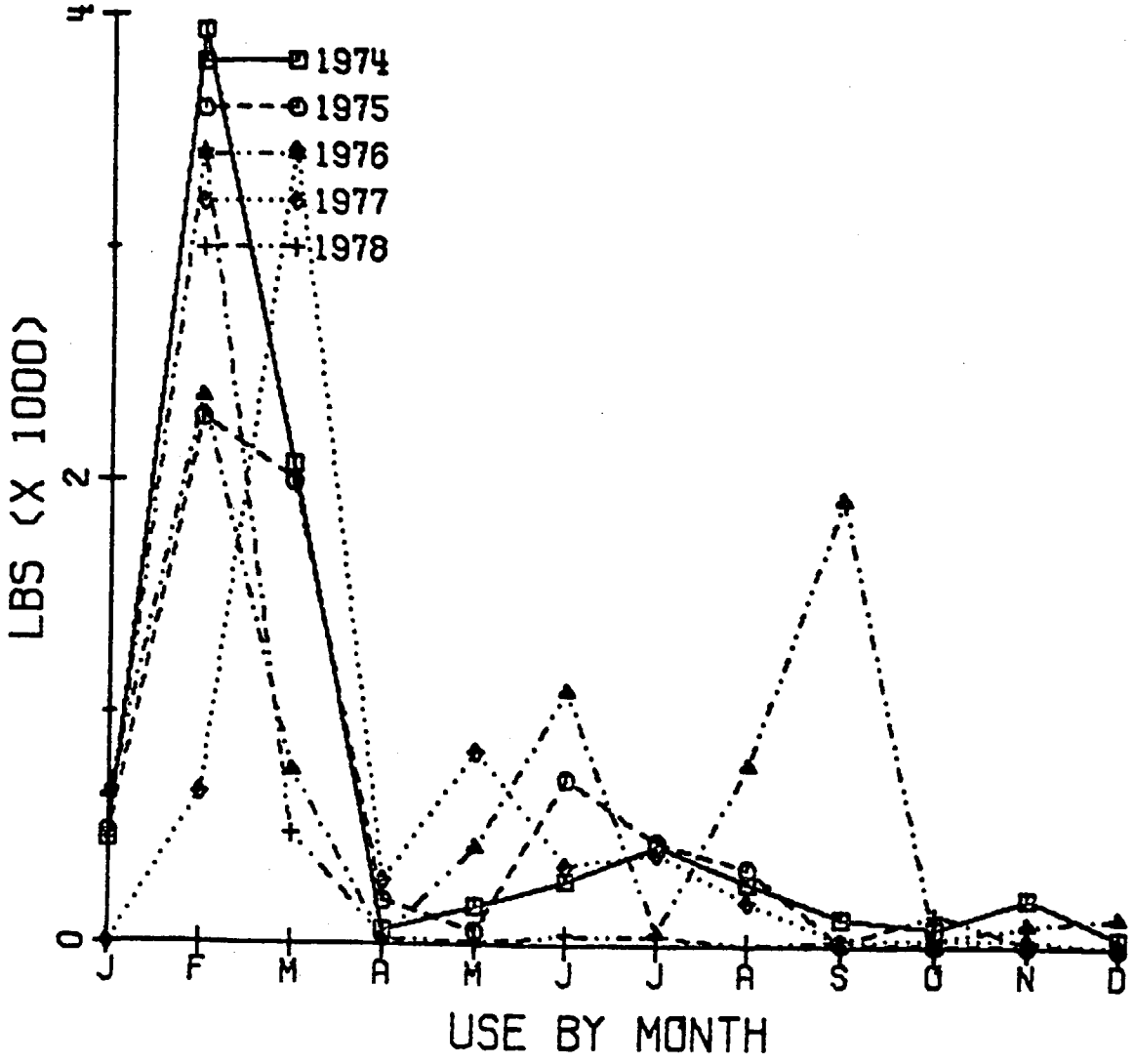


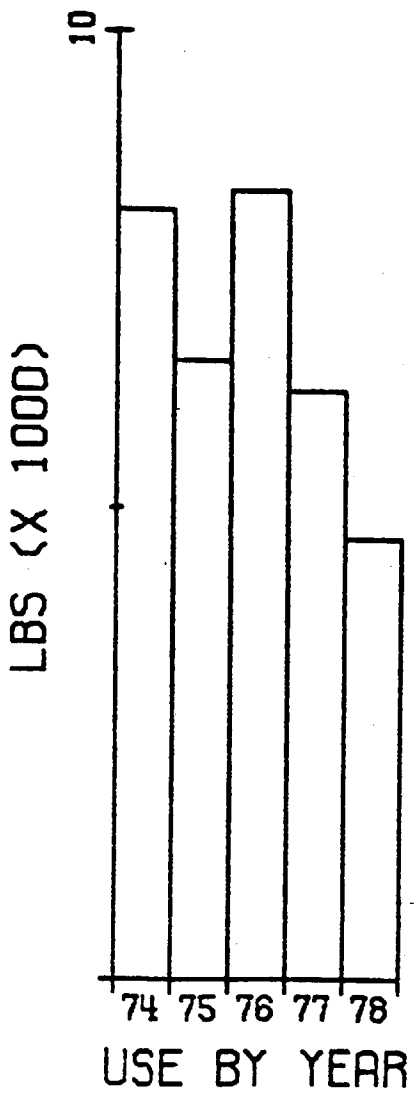
USE OF 2,4-D (ALL FORMS) IN GLENN COUNTY



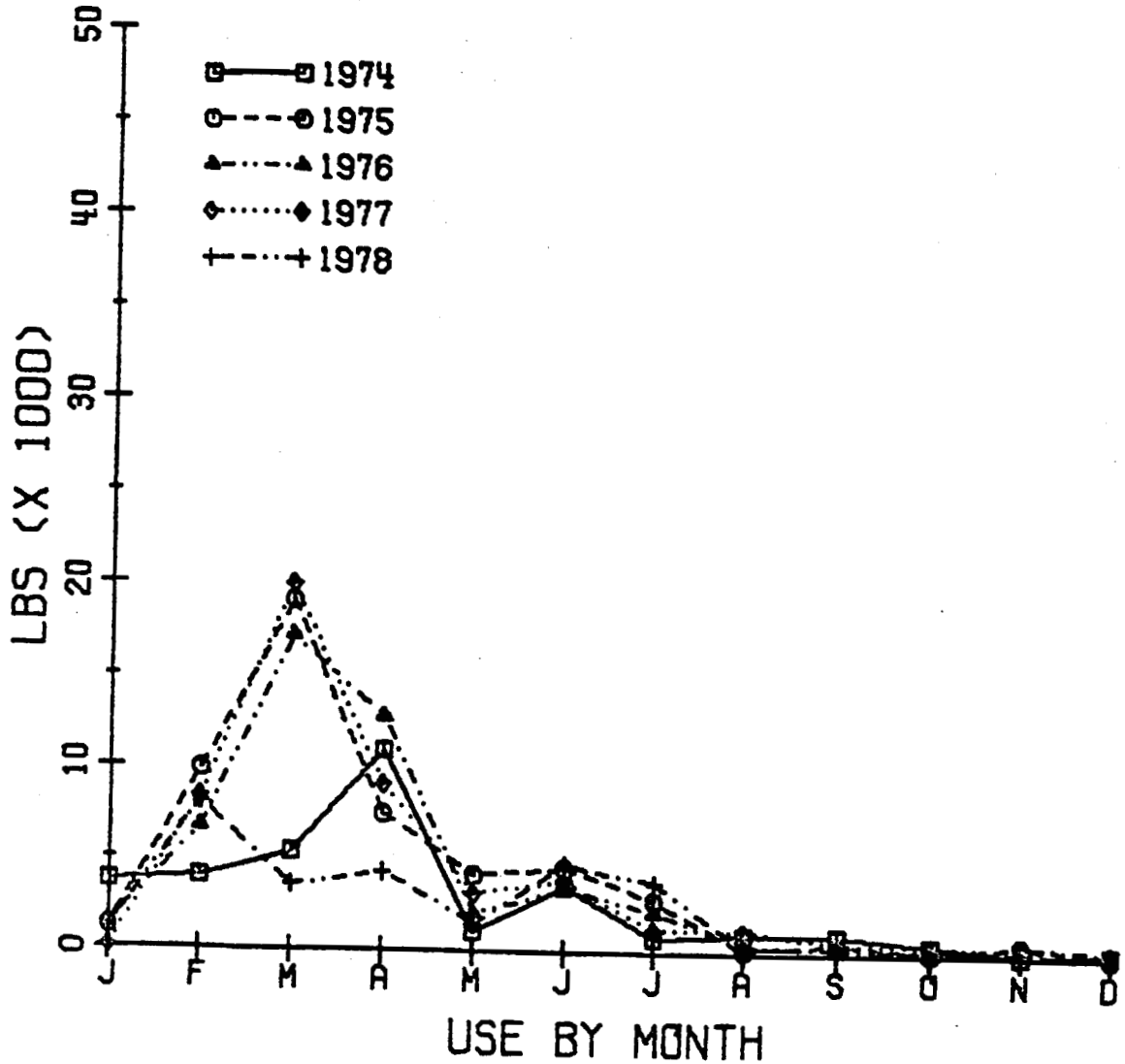


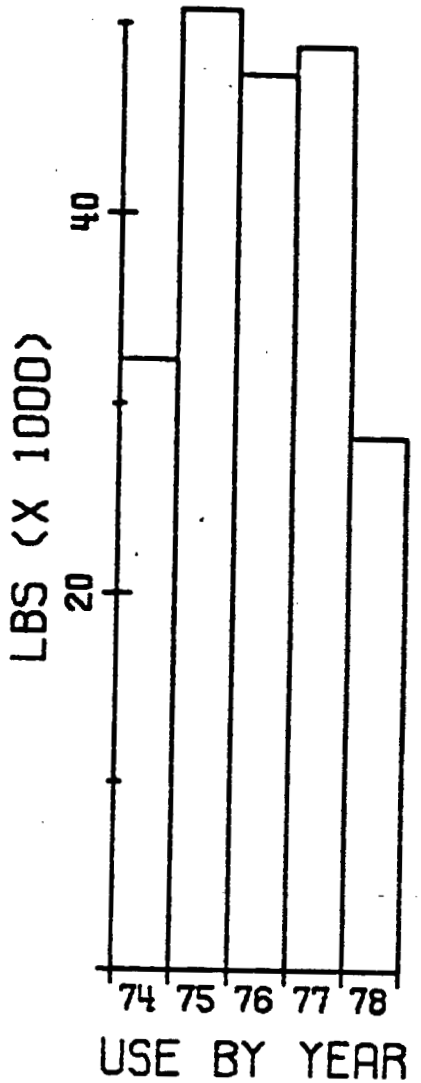
USE OF 2,4-D (ALL FORMS) IN PLACER COUNTY



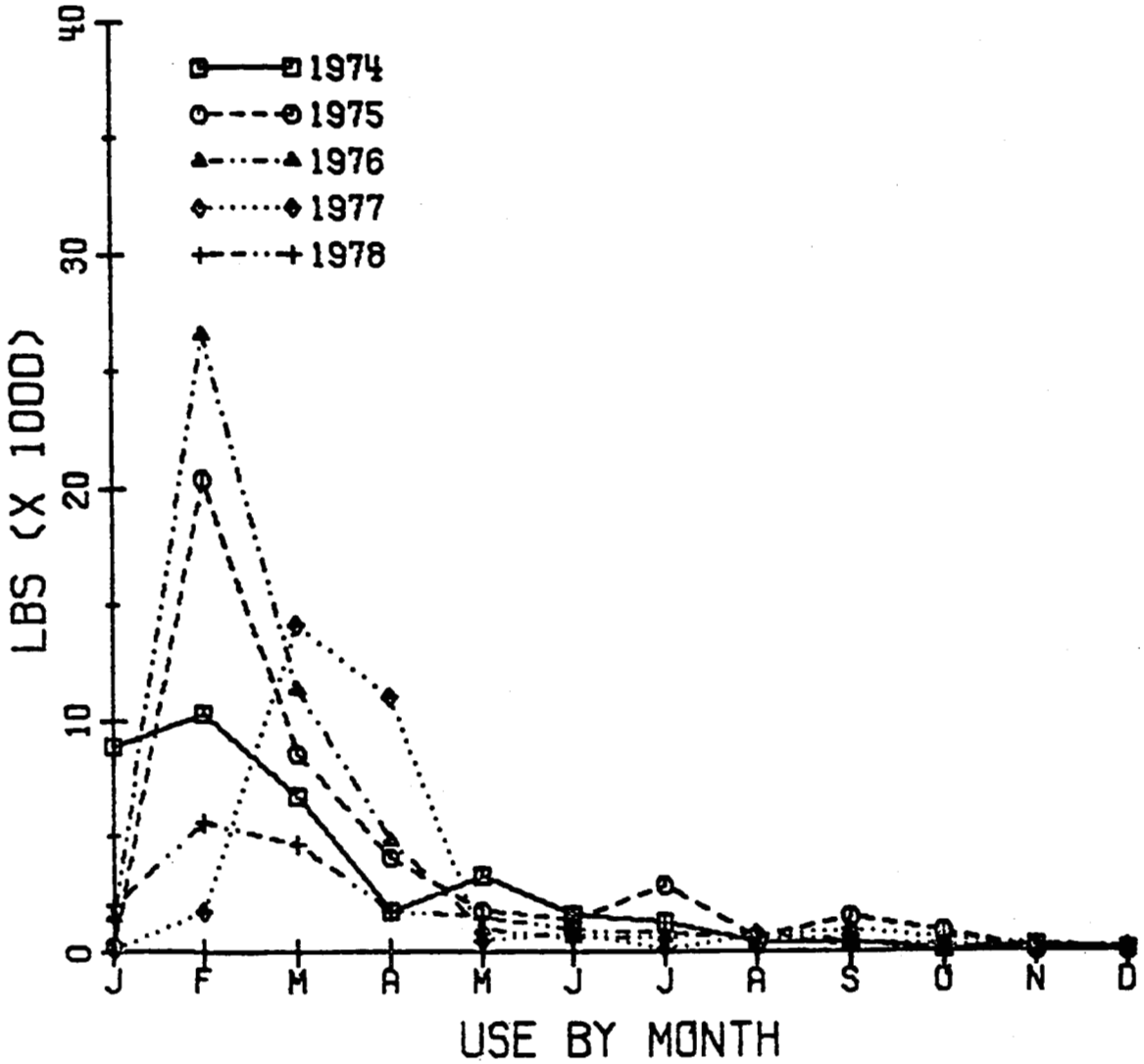


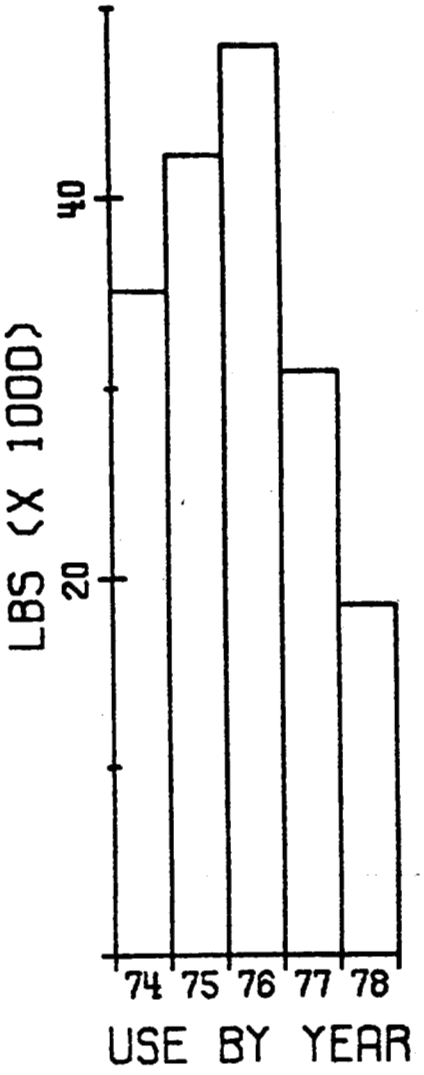
USE OF 2,4-D (ALL FORMS) IN SACRAMENTO COUNTY



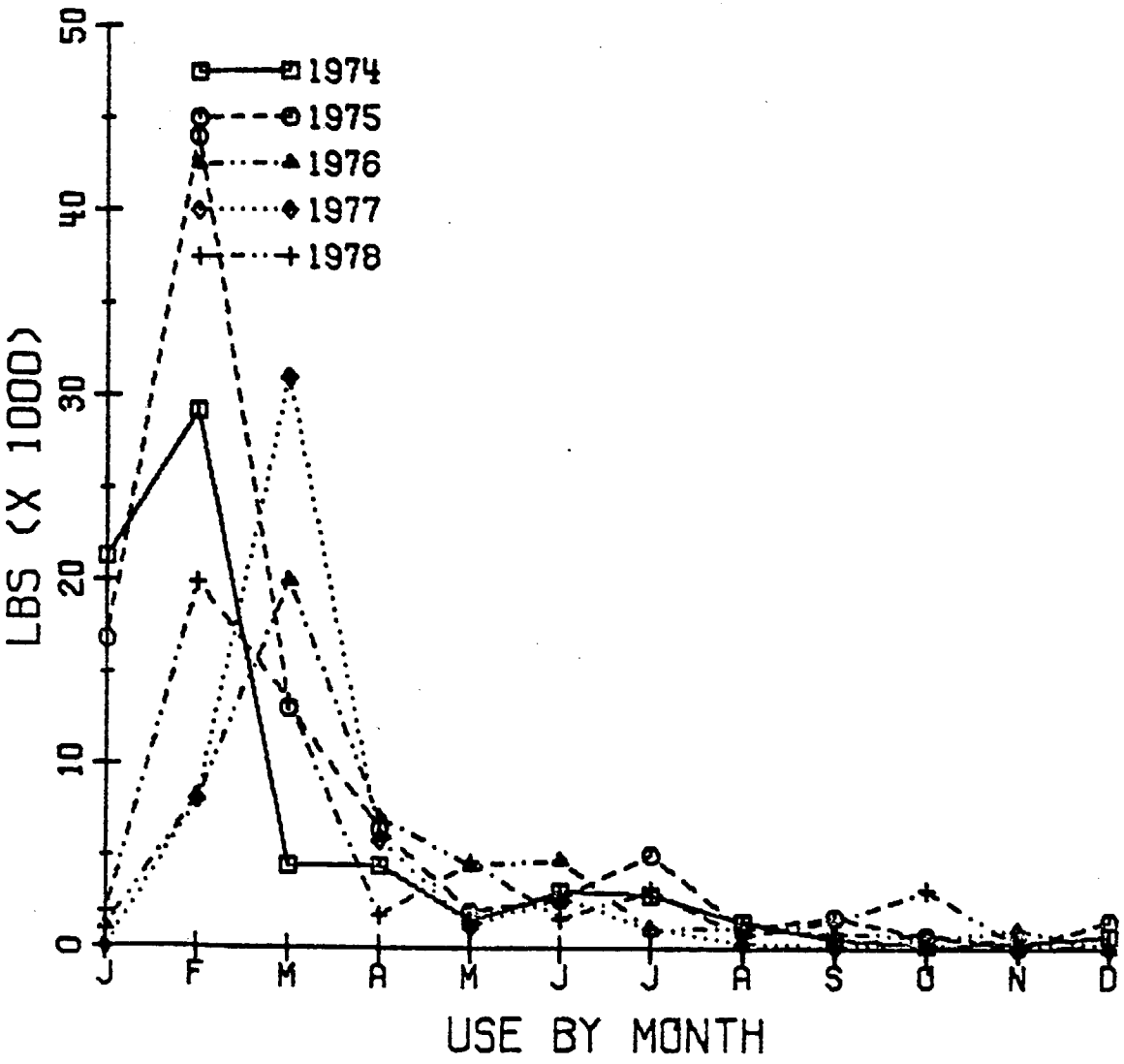


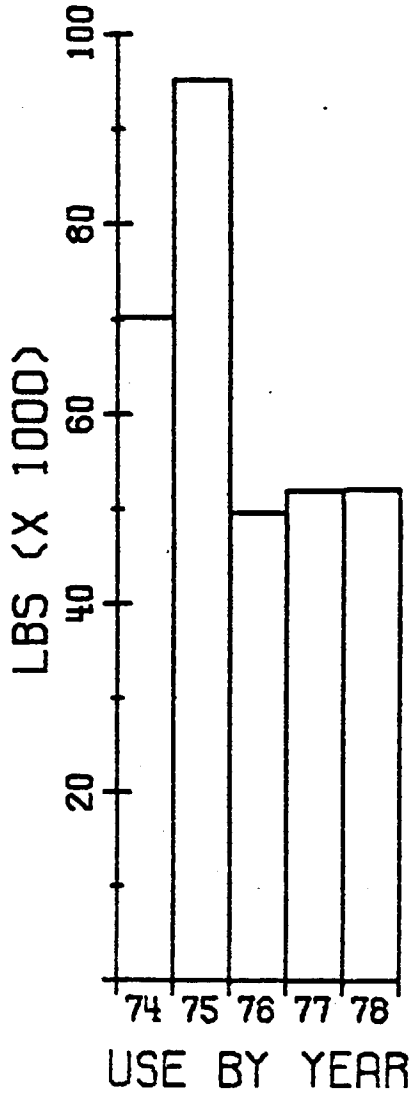
USE OF 2,4-D (ALL FORMS) IN SUTTER COUNTY



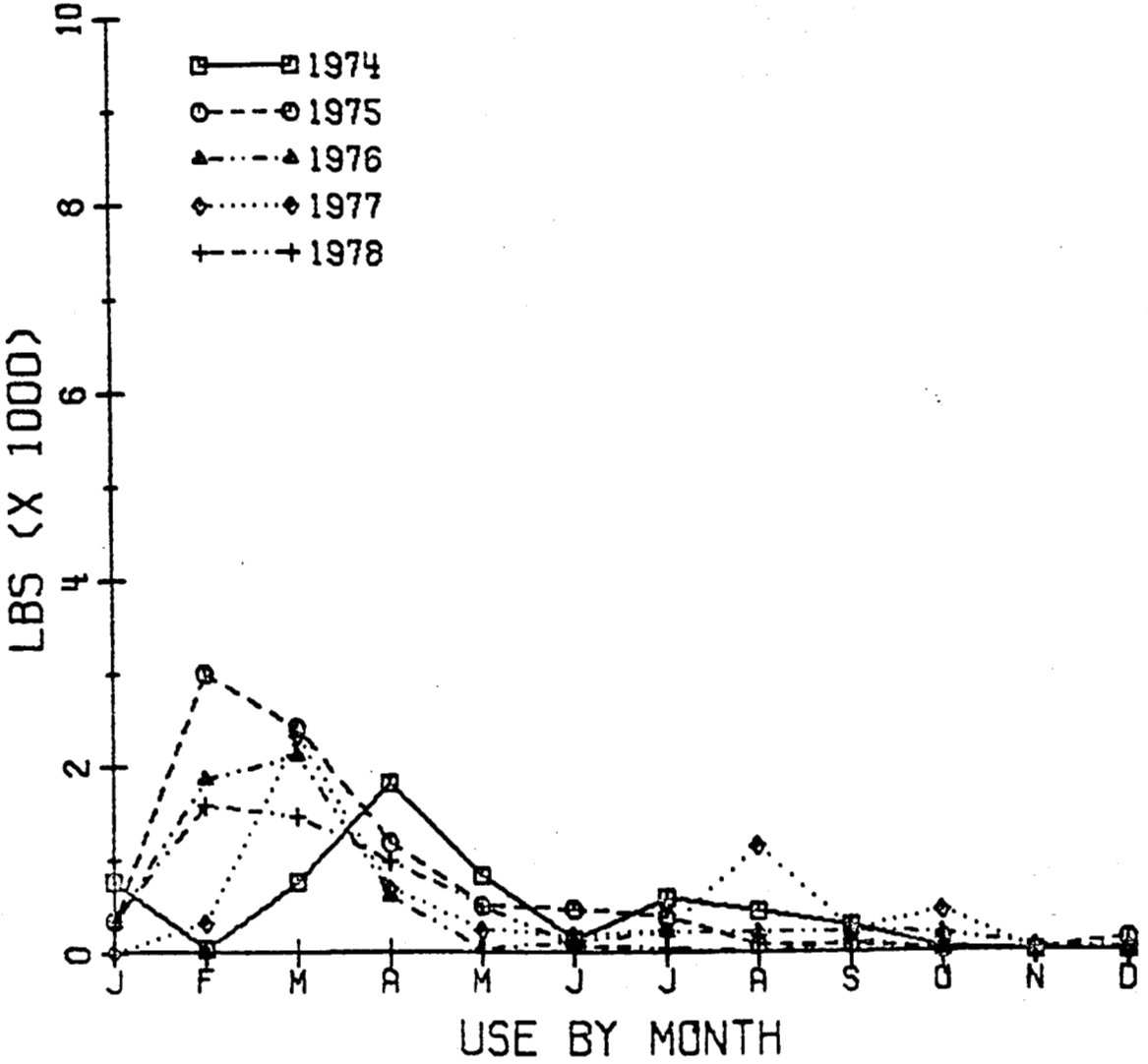


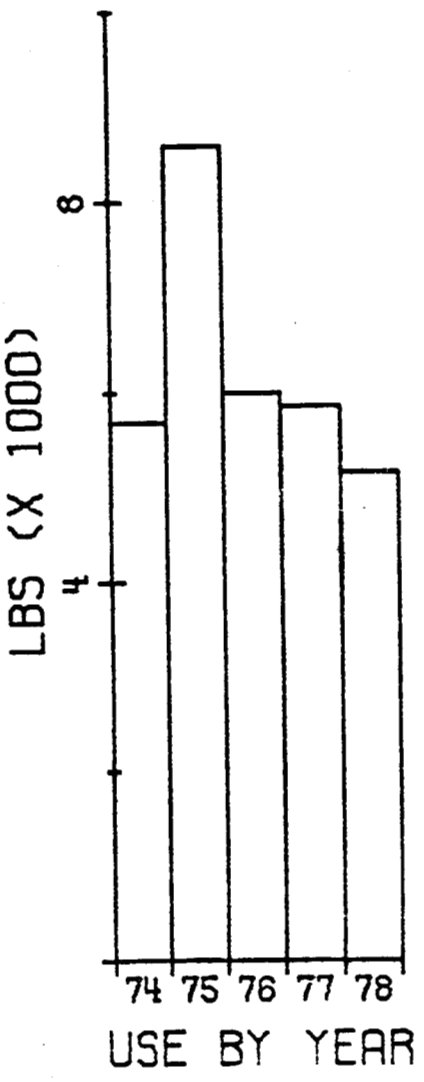
USE OF 2,4-D (ALL FORMS) IN YOLO COUNTY





USE OF 2,4-D (ALL FORMS) IN YUBA COUNTY





Appendix V

TOTAL POUNDS OF ALL FORMS OF 2,4-D USED IN EIGHT CALIFORNIA COUNTIES BY MONTH AND YEAR, 1974 - 78

TOTAL POUNDS OF

2,4-D (ALL USAGE)

00636 00980 00981 00801 00802 01255 00803 00804 00805 00875
00806 01259 00807 01622 01962 00809 00810 00811 01032 01096
01999 01275 00812 00813 00814 00815 01138 00816

USED IN COUNTIES OF CALIFORNIA

BY MONTHS OF 1974

MONTH / COUNTY	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	TOTAL
BUTTE	3884	4996	2869	4952	1137	1517	1151	652	146	303	5	9	21620
COLUSA	8022	24280	10565	24388	2172	1006	1097	916	332	1339	157	55	74327
GLENN	2947	6224	4685	62945	1363	482	320	360	56	214	9995	0	89591
PLACER	452	3940	2072	62	171	279	433	274	122	76	207	40	8128
SACRAMENTO	3686	3984	5357	11032	1120	3566	846	1037	1048	445	14	177	32311
SUTTER	8912	10293	6752	1724	3306	1580	1257	433	400	75	265	72	35069
YOLO	21296	29199	4515	4508	1529	3148	2885	1447	475	218	274	675	70168
YUBA	768	41	753	1815	830	147	578	437	273	36	0	0	5679
TOTAL	49967	82958	37568	111425	11628	11725	8566	5556	2851	2706	10916	1027	336892

TOTAL POUNDS OF

2,4-D (ALL USAGE)

00636 00980 00981 00801 00802 01255 00803 00804 00805 00875
00806 01259 00807 01622 01962 00809 00810 00811 01032 01096
01999 01275 00812 00813 00814 00815 01138 00816

USED IN COUNTIES OF CALIFORNIA

BY MONTHS OF 1975

MONTH / COUNTY	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	TOTAL
BUTTE	22	11991	7257	7905	1441	556	1593	122	1004	98	131	108	32228
COLUSA	1288	26680	32924	8171	1456	3677	4014	2557	3267	104	326	248	84711
GLENN	583	36886	14145	4990	573	503	623	594	277	299	55	0	59529
PLACER	482	2272	2002	190	63	723	446	333	12	7	9	0	6540
SACRAMENTO	1217	9935	19079	7488	4207	4605	2870	183	515	82	558	36	50772
SUTTER	230	20380	8568	4044	1795	1395	2881	632	1514	856	0	0	42296
YOLO	16776	44024	13084	6533	1975	2742	5090	1096	1691	659	81	1513	95266
YUBA	333	2999	2414	1174	507	458	383	80	84	23	0	150	8605
TOTAL	20931	155167	99473	40495	12017	14660	17900	5597	8365	2129	1155	2056	379946

TOTAL POUNDS OF

2,4-D (ALL USAGE)

00636 00980 00981 00801 00802 01255 00803 00804 00805 00875
00806 01259 00807 01622 01962 00809 00810 00811 01032 01096
01999 01275 00812 00813 00814 00815 01138 00816

USED IN COUNTIES OF CALIFORNIA

BY MONTHS OF 1976

MONTH / COUNTY	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	TOTAL
BUTTE	4144	6651	8172	7922	298	417	349	814	89	48	2	30	28936
COLUSA	945	7265	19801	6863	2902	2572	2136	3975	1116	546	818	27	48966
GLENN	8484	1999	8880	1313	1094	1591	632	132	126	137	381	431	25201
PLACER	642	2363	752	21	423	1104	58	784	1937	31	93	128	8336
SACRAMENTO	1433	6694	17155	12777	2093	3453	2210	421	252	38	560	292	47378
SUTTER	1547	26588	11352	4813	963	611	643	801	417	7	255	126	48123
YOLO	1102	8224	20024	7100	4508	4760	1007	1163	774	729	231	35	49656
YUBA	320	1860	2120	606	38	109	223	213	223	204	48	36	6002
TOTAL	18617	61645	88256	41415	12318	14618	7258	8304	4935	1740	2387	1106	262599

TOTAL POUNDS OF

2,4-D (ALL USAGE)

00636 00980 00981 00801 00802 01255 00803 00804 00805 00875
00806 01259 00807 01622 01962 00809 00810 00811 01032 01096
01999 01275 00812 00813 00814 00815 01138 00816

USED IN COUNTIES OF CALIFORNIA

BY MONTHS OF 1977

MONTH / COUNTY	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	TOTAL
BUTTE	3	2986	12942	8558	546	280	67	180	5	18645	442	64	44718
COLUSA	47	5260	31290	5504	1561	10343	438	442	565	289	425	0	56164
GLENN	0	2713	25344	5935	610	903	516	420	10	316	0	8	36774
PLACER	0	658	3415	281	841	346	398	190	22	35	29	0	6214
SACRAMENTO	138	8367	20003	9082	3244	3864	1289	1242	577	416	418	280	48919
SUTTER	118	1742	14121	11012	505	800	137	715	945	570	276	0	30941
YOLO	2	8074	31000	5939	1200	2766	1069	290	78	524	1037	38	52018
YUBA	0	327	2341	690	249	173	239	1138	239	446	0	13	5854
TOTAL	309	30127	140456	47001	8756	19475	4151	4616	2440	21242	2627	402	281601

TOTAL POUNDS OF

2,4-D (ALL USAGE)

00636 00980 00981 00801 00802 01255 00803 00804 00805 00875
00806 01259 00807 01622 01962 00809 00810 00811 01032 01096
01999 01275 00812 00813 00814 00815 01138 00816

USED IN COUNTIES OF CALIFORNIA

BY MONTHS OF 1978

MONTH / COUNTY	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	TOTAL
BUTTE	1266 0	5505 0	4669 5241	4768	79 79	287 0	45 361	315 0	393 393	0 13	5	0 0	20354 10861
COLUSA	1044 0	16052 394	12532 14299	6012	1345 1008	2472 607	15681 14978	340 340	296 369	232 232	0	5 0	56011 38240
GLENN	228 0	9009 0	26176 27876	296	1431 476	310 1044	1070 26	0 149	377 228	5 5	42	5 5	38929 30146
PLACER	425 0	3415 0	480 480	29	13 20	44 1	42 34	2 2	24 24	139 139	14	0 0	4677 744
SACRAMENTO	1071 0	5134 0	3568 4022	4326	1549 1611	4781 363	3813 3524	336 179	329 329	149 149	199	41 41	28296 14742
SUTTER	1990 0	5598 471	4650 5022	1752	1530 1523	433 36	844 911	588 606	315 188	274 274	121	0 0	18595 10902
YOLO	1933 142	14879 390	13448 13535	1815	4705 4789	1638 417	3162 2683	726 494	1504 1313	3194 3821	178	2 2	52174 29579
YUBA	351 0	1580 90	1465 2522	985	497 38	71 0	45 14	1 109	115 7	14 14	24	3 3	5151 3807
TOTAL	142	1345	72998	19983	9544	2468	22531	1880	2851	4646	582	51	139021

TOTAL POUNDS OF

2,4-D (ALL USAGE)

00636 00980 00981 00901 00802 01255 00803 00804 00805 00875
00806 01259 00807 01622 01962 00809 00810 00811 01032 01096
01999 01275 00812 00813 00814 00815 01138 00816

USED IN COUNTIES OF CALIFORNIA

BY MONTHS OF 1974

MONTH / COUNTY	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	TOTAL
BUTTE	3884	4996	2869	4952	1137	1517	1151	652	146	303	5	9	21620
COLUSA	8022	24280	10565	24388	2172	1006	1097	916	332	1339	157	55	74327
GLENN	2947	6224	4685	62945	1363	482	320	360	56	214	9995	0	89591
PLACER	452	3940	2072	62	171	279	433	274	122	76	207	40	8128
SACRAMENTO	3686	3984	5357	11032	1120	3566	846	1037	1048	445	14	177	32311
SUTTER	8912	10293	6752	1724	3306	1580	1257	433	400	75	265	72	35069
YOLO	21296	29199	4515	4508	1529	3148	2885	1447	475	218	274	675	70168
YUBA	768	41	753	1815	830	147	578	437	273	36	0	0	5679
TOTAL	49967	82958	37568	111425	11628	11725	8566	5556	2851	2706	10916	1027	336892

TOTAL POUNDS OF

2,4-D (ALL USAGE)

00636 00980 00981 00801 00802 01255 00803 00804 00805 00875
00806 01259 00807 01622 01962 00809 00810 00811 01032 01096
01999 01275 00812 00813 00814 00815 01138 00816

USED IN COUNTIES OF CALIFORNIA

BY MONTHS OF 1975

MONTH / COUNTY	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	TOTAL
BUTTE	22	11991	7257	7905	1441	556	1593	122	1004	98	131	108	32228
COLUSA	1288	26680	32924	8171	1456	3677	4014	2557	3267	104	326	248	84711
GLENN	583	36886	14145	4990	573	503	623	594	277	299	55	0	59529
PLACER	482	2272	2002	190	63	723	446	333	12	7	9	0	6540
SACRAMENTO	1217	9935	19079	7488	4207	4605	2870	183	515	82	554	36	50772
SUTTER	230	20380	8568	4044	1795	1395	2881	632	1514	856	0	0	42296
YOLO	16776	44024	13084	6533	1975	2742	5090	1096	1691	659	81	1513	95266
YUBA	333	2999	2414	1174	507	458	383	80	84	23	0	150	8603
TOTAL	20931	155167	99473	40495	12017	14660	17900	5597	8365	2129	1155	2056	379946

TOTAL POUNDS OF

2,4-D (ALL USAGE)

00636 00980 00981 00801 00802 01255 00803 00804 00805 00875
00806 01259 00807 01622 01962 00809 00810 00811 01032 01096
01999 01275 00812 00813 00814 00815 01138 00816

USED IN COUNTIES OF CALIFORNIA

BY MONTHS OF 1976

MONTH / COUNTY	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	TOTAL
BUTTE	4144	6651	8172	7922	298	417	349	814	89	48	2	30	28936
COLUSA	945	7265	19801	6863	2902	2572	2136	3975	1116	546	818	27	48966
GLENN	8484	1999	8880	1313	1094	1591	632	132	126	137	381	431	25201
PLACER	642	2363	752	21	423	1104	58	784	1937	31	93	128	8336
SACRAMENTO	1433	6694	17155	12777	2093	3453	2210	421	252	38	560	292	47378
SUTTER	1547	26588	11352	4813	963	611	643	801	417	7	255	126	48123
YOLO	1102	8224	20024	7100	4508	4760	1007	1163	774	729	231	35	49656
YUBA	320	1860	2120	606	38	109	223	213	223	204	48	36	6002
TOTAL	18617	61645	88256	41415	12318	14618	7258	8304	4935	1740	2387	1106	262599

TOTAL POUNDS OF

2,4-D (ALL USAGE)

00636 00980 00981 00801 00802 01255 00803 00804 00805 00875
00806 01259 00807 01622 01962 00809 00810 00811 01032 01096
01999 01275 00812 00813 00814 00815 01138 00816

USED IN COUNTIES OF CALIFORNIA

BY MONTHS OF 1977

MONTH / COUNTY	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	TOTAL
BUTTE	3	2986	12942	8558	546	280	67	180	5	18645	442	64	44718
COLUSA	47	5260	31290	5504	1561	10343	438	442	565	289	425	0	56164
GLENN	0	2713	25344	5935	610	903	516	420	10	316	0	8	36774
PLACER	0	658	3415	281	841	346	398	190	22	35	29	0	6214
SACRAMENTO	138	8367	20003	9082	3244	3864	1289	1242	577	416	418	280	48919
SUTTER	118	1742	14121	11012	505	800	137	715	945	570	276	0	30941
YOLO	2	8074	31000	5939	1200	2766	1069	290	78	524	1037	38	52018
YUBA	0	327	2341	690	249	173	239	1138	239	446	0	13	5854
TOTAL	309	30127	140456	47001	8756	19475	4151	4616	2440	21242	2627	402	281601

TOTAL POUNDS OF

2,4-D (ALL USAGE)

00636 00980 00981 00801 00802 01255 00803 00804 00805 00875
00806 01259 00807 01622 01962 00809 00810 00811 01032 01096
01999 01275 00812 00813 00814 00815 01138 00816

USED IN COUNTIES OF CALIFORNIA

BY MONTHS OF 1978

MONTH / COUNTY	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	TOTAL
BUTTE	1269 0	5505 0	4669 5241	4768	79 79	287 0	45 361	315 0	393 393	0 13	5	0 0	20354 10861
COLUSA	1044 0	16052 394	12532 14299	6012	1345 1008	2472 607	15681 14978	340 340	296 369	232 232	0	5 0	56011 38240
GLENN	205 0	9009 0	26176 27876	296	1431 476	310 1044	1070 26	0 149	377 228	5 5	42	5 5	38121 30146
PLACER	475 0	3415 0	480 480	29	13 20	44 1	42 34	2 2	24 24	139 139	14	0 0	4677 744
SACRAMENTO	1071 0	5134 0	3568 4022	4326	1549 1611	4781 363	3813 3524	336 179	329 329	149 149	199	41 41	28296 14742
SUTTER	1990 0	5598 471	4660 5022	1752	1530 1523	433 36	844 911	588 606	315 188	274 274	121	0 0	18595 10902
YOLO	1923 142	14879 390	13448 13535	1815	4705 4789	1638 417	3162 2683	726 494	1504 1313	2194 3821	178	2 2	52174 29579
YUBA	351 0	1680 90	1465 2522	985	497 38	71 0	45 14	1 109	115 7	14 14	24	3 3	5151 3807
TOTAL	142	1345	72998	19983	9544	2468	22531	1880	2851	4646	582	51	139021

Appendix VI

TABLE A-I RESULTS OF HI-VOL AIR SAMPLING, JUNE 17, 1979

(JOHNSON RICE)

TABLE A-II RESULTS OF HI-VOL AIR SAMPLING, JUNE 22, 1979

(SKINNER RICE)

TABLE A-III RESULTS OF HI-VOL AIR SAMPLING, JUNE 30, 1979

(SKINNER RICE)

See text of Part IV for experimental conditions.

Table A-I. June 17 (Johnson rice).

Time	High Orchard[a] Amount, ng	Air Volume Sampled, m^3	Conc. in Air, ng/m^3	Sampling Period	Low Orchard[a] Amount ng	Air Volume Sampled, m^3	Conc. in Air, ng/m^3	Sampling Period
1 hour	MCPA 1,456	110.9	13	0845-1021	-	-	-	-
	4-CLOC 20,250		183		-		-	
2 hours	-	-	-	-	-	-	-	-
	-		-		-		-	
5 hours	< 200	134.4	< 2	1240-1440	< 200	134.4	< 2	1240-1440
	14,400		107		10,550		78	
1 day	890	60.5	15	1309-1403	565	60.5	9	1309-1403
	11,050		183		730		12	
2 days	260	70.6	4	1618-1721	960	70.6	14	1618-1721
	730		10		700		10	

[a]Price orchard at canopy top and 1.2 m above orchard floor.

Table A-I, cont.

Time	South Edge of Price Orchard: Amount, ng	Air Volume Sampled, m^3	Conc. in Air, ng/m^3	Sampling Period	South Edge of Rice Field (0.3 m high)[b]: Amount ng	Air Volume Sampled, m^3	Conc. in Air, ng/m^3	Sampling Period
1 hour MCPA	1,993	110.9	17	0845-1021	-	-	-	-
1 hour 4-CLOC	22,158		200		-		-	
2 hours	-	-	-	-	1,875	142.2	13	0945-1152
	-		-		24,200		170	
5 hours	1,050	134.4	8	1240-1440	2,175	127.7	17	1300-1454
	20,100		150		< 200		< 2	
1 day	2,326	67.2	35	1312-1412	4,400	67.2	65	1251-1351
	26,300		391		16,800		250	
2 days	400	70.6	6	1624-1727	1,730	110.9	16	1606-1745
	1,050		15		2,500		22	

[b]Sampler moved into treated field on days 1 and 2.

Table A-I, cont.

	South Edge of Rice Field (1.8 m high)[c]				201 m South of Rice Field			
Time	Amount, ng	Air Volume Sampled, m^3	Conc. in Air, ng/m^3	Sampling Period	Amount ng	Air Volume Sampled, m^3	Conc. in Air, ng/m^3	Sampling Period
2 hours	MCPA 2,250 4-CLOC 16,250	142.2	16 114	0945-1152	1,312 31,200[d]	110.9	12 281	1012-1151
5 hours	1,088 < 200	127.7	8 < 2	1300-1454	340 3,250	134.4	3 24	1303-1503
1 day	1,220 13,850	67.2	18 206	1251-1351	1,745 16,800	73.9	24 227	1236-1342
2 days	1,290 830	110.9	12 8	1606-1745	- -	-	- -	-

[c]Sampler moved into treated field on days 1 and 2.

[d]4-CLOC confirmed by GC/MS.

Table A-I, cont.

	563 m South of Rice Field				1931 m South of Rice Field			
Time	Amount, ng	Air Volume Sampled, m^3	Conc. in Air, ng/m^3	Sampling Period	Amount ng	Air Volume Sampled, m^3	Conc. in Air, ng/m^3	Sampling Period
1 hour MCPA	-	-	-	-	538	174.7	3	0830-1106
1 hour 4-CLOC	-		-		11,650		67	
5 hours	< 200	144.5	< 2	1303-1512	460	141.1	3	1312-1518
	< 200		< 2		2,233		16	
1 day	960	87.4	11	1218-1336	< 200	94.1	< 2	1200-1324
	13,700		157		13,250		141	

Table A-II. June 22 (Skinner rice). Appendix VII

Time	High Orchard[a] Amount, ng	Air Volume Sampled, m^3	Conc. in Air, ng/m^3	Sampling Period	Low Orchard[a] Amount ng	Air Volume Sampled, m^3	Conc. in Air, ng/m^3	Sampling Period
Spray MCPA	288	98.6	3	0817-0945	281	98.6	3	0817-0945
Spray 4-CLOC	315		3		5,170		52	
1 hour	< 200	171.4	< 2	1145-1421	< 300	171.4	< 2	1145-1421
	< 200		< 2		2,094		12	
5 hours	< 200	124.3	< 2	1421-1618	< 200	124.3	< 2	1421-1618
	< 200		< 2		< 222		< 2	
1 day[b,c] MCPA	1,420 / 7,200	107.5 / 67.2	13 / 107	1021-1200 / 1424-1524	674	67.2	10	1424-1524
1 day[b,c] 4-CLOC	< 200 / 18,500		< 2 / 275		816		12	
3 days	< 200	80.6	< 3	1109-1224	800	90.7	9	1106-1230
	875		11		7,275		80	

[a] High Orchard: at top of orchard canopy (McClintock) 30 m in from south edge.
Low Orchard: 1.2 m above orchard floor next to High Orchard.

[b] High Orchard data reported as morning (upper numbers) and afternoon (lower numbers).

[c] Afternoon MCPA and 4-CLOC confirmed by GC/MS.

Table A-II, cont.

Time	North Edge of Rice Field[d] Amount, ng	Air Volume Sampled, m^3	Conc. in Air, ng/m^3	Sampling Period	South Edge of Rice Field[d] Amount ng	Air Volume Sampled, m^3	Conc. in Air, ng/m^3	Sampling Period
Spray MCPA	26,000	125.4	207	0817-1009	82,800	144.5	573	0833-1042
Spray 4-CLOC	2,610		21		17,600		122	
1 hour	1,050	184.8	6	1148-1436	28,050[f]	205.0	137	1206-1509
	10,550		57		18,150[f]		88	
5 hours	980	100.8	10	1442-1618	17,850[g]	77.3	231	1521-1633
	< 200		< 2		8,775[g]		114	
1 day[e] MCPA	4,075 / 2,350	107.5 / 67.2	38 / 35	1000-1136 / 1430-1530	-	-	-	-
1 day[e] 4-CLOC	2,175 / 1,988		20 / 30		-		-	
3 days	490	90.7	5	1057-1218	-	-	-	-
	2,225		24		-		-	

[d] Both stations were approximately 7.6 m north and south.

[e] North Edge data reported as morning (upper numbers) and afternoon (lower numbers).

[f] MCPA: 23,100 ng, 33,000 ng; 4-CLOC; 14,400 ng, 21,900 ng.

[g] MCPA: 17,800 ng, 17,900 ng; 4-CLOC: 6,750 ng, 10,800 ng.

Table A-II, cont.

	201 m South of Rice Field				402 m South of Rice Field			
Time	Amount, ng	Air Volume Sampled, m^3	Conc. in Air, ng/m^3	Sampling Period	Amount ng	Air Volume Sampled, m^3	Conc. in Air, ng/m^3	Sampling Period
Spray MCPA	47,200	160.2	295	0837-1100	10,850	174.7	62	0839-1115
Spray 4-CLOC	3,180		20		1,210		7	
1 hour	12,250	208.3	59	1212-1518	1,026	218.4	5	1218-1533
1 hour	9,600		46		5,342		24	
5 hours	4,850	70.6	69	1541-1644	-	-	-	-
5 hours	7,150		101		-		-	

Table A-II, cont.

Time		0.3 m Above Rice Field				1.8 m Above Rice Field			
		Amount, ng	Air Volume Sampled, m^3	Conc. in Air, ng/m^3	Sampling Period	Amount ng	Air Volume Sampled, m^3	Conc. in Air, ng/m^3	Sampling Period
1 day[h]	MCPA	3,298 / 5,300	104.2 / 67.2	32 / 79	0951-1124 / 1445-1545	3,460 / 3,975	104.2 / 67.2	33 / 59	0951-1124 / 1445-1545
	4CLOC	4,600 / 4,133		44 / 62		<200 / 2,112		<2 / 31	
3 days		720 / 1,620	73.9	10 / 22	1051-1157	720 / 1,580	73.9	10 / 21	1051-1157

[h] 0.3 m and 1.8 m data reported as morning (upper numbers) and afternoon (lower numbers).

Table A-III. June 10 (Skinner rice).

Location	Spray				0.5-1 hour			
	Amount, ng	Air Volume Sampled, m^3	Conc. in Air, ng/m^3	Sampling Period	Amount ng	Air Volume Sampled, m^3	Conc. in Air, ng/m^3	Sampling Period
NW Orchard High[a] MCPA	< 200	77.3	< 3	1009-1118	-	-	-	-
NW Orchard High[a] 4-CLOC	11,100		144		-		-	
NW Orchard Low[a]	1,050	94.1	11	1118-1242	610	252.0	2	1255-1640
NW Orchard Low[a]	17,900		190		10,000		40	
North Orchard[b,c]	960	206.1	5	1008-1312	-	-	-	-
North Orchard[b,c]	12,325		60		-		-	
N. Edge of Rice Field	8,500	185.9	46	1008-1254	1,770	168.0	10	1315-1545
N. Edge of Rice Field	9,100		49		8,550		51	
S. Edge of Rice Field (7.6 m)	46,500[d]	134.4	346	1000-1200	5,788[e]	127.7	45[f]	1212-1406
S. Edge of Rice Field (7.6 m)	10,375[d]		77		11,262[e]		88[f]	

[a] McClintock orchard at canopy top and 1.2 m above orchard floor.

[b] Martinez orchard; MCPA average of 990 ng and 930 ng; 4-CLOC average of 12,150 ng and 12,500 ng.

[c] MCPA and 4-CLOC confirmed by GC/MS.

[d] MCPA: 54,400 ng, 38,600 ng; 4-CLOC: 13,000 ng, 7,750 ng.

[e] MCPA: 5,825 ng, 5,750 ng; 4-CLOC: 13,725 ng, 8,800 ng.

[f] Samplers shut off prematurely; conc's are actually greater.

Table A-III, cont.

	Spray				0.5-1 hour			
Location	Amount, ng	Air Volume Sampled, m^3	Conc. in Air, ng/m^3	Sampling Period	Amount ng	Air Volume Sampled, m^3	Conc. in Air, ng/m^3	Sampling Period
201 m South of Rice Field	6,900	134.4	51[g]	1012-1212	870	171.4	5	1215-1448
	7,650		57[g]		12,950		76	
402 m South of Rice Field	2,556[h]	141.1	18	1012-1218	2,151[i]	184.8	12	1224-1509
	10,175[h]		72		10,612[i]		57	

[g]Samplers shut off prematurely; conc's are actually greater.

[h]MCPA: 2,512 ng, 2,600 ng; 4-CLOC: 10,250 ng, 10,100 ng.

[i]MCPA: 2,362 ng, 1,940 ng; 4-CLOC: 10,400 ng, 10,825 ng.